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Routes towards an abstract thermodynamics in the late nineteenth century

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Abstract. Two different traditions of research emerged from Rudolf Clausius's version of thermodynamics. While James Clerk Maxwell and Ludwig Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, others relied on a macroscopic and more abstract approach that set aside specific mechanical models. This second approach blossomed in about two decades in different countries of Europe and in the United States. François Massieu, Josiah Willard Gibbs, Hermann Helmholtz, and then Pierre Duhem explored the connections between the contents of thermodynamics and the formal structures of analytical mechanics. Others like the young Max Planck and Arthur von Oettingen pursued a sort of formal symmetry between thermal and mechanical variables. In the British Isles, Joseph John Thomson developed a *dynamical* approach to physics and chemistry, making use of the tools of abstract mechanics without excluding microscopic motions. Some developments were logically interconnected, as it was for Massieu's, Gibbs's, Helmholtz's, and Duhem's, even though they occurred in a largely independent manner. Duhem put forward the most original and most systematic reinterpretation of thermodynamics, which involved a bold upgrading of analytical mechanics and a bold mathematical unification of physics and chemistry. A strong commitment to unification was one of the hallmarks of all these theoretical researches.

Introduction

In this journal, Ingo Müller and Wolf Weiss have recently discussed different trends and different stages in the history of thermodynamics of irreversible processes, where successive generations of scientists attempted to incorporate "Fourier's law and the law of Navier-Stokes into a consistent thermodynamic scheme" [Müller and Weiss 2012, pp. 180-4; Müller 2007, p. 244]. The purpose of the present study is to focus on the first stages of that history and to highlight aspects that are not generally known to physicists.

In the last decades of the nineteenth century, electromagnetic theories had already translated into fruitful technologies, which were deeply transforming the occidental

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way of life. The new age of electromagnetism, whose symbolic device was the electromagnetic machine, seemed to supplant, at least in part, the old age of smoky thermal engines. Meanwhile, in the 1860s and 1870s, the recently emerged thermodynamics branched out into two different directions: the refinement of the kinetic theory of gases as a questionable alliance between mechanical laws 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. Thanks to Joseph-Louis Lagrange and his *Mécanique analytique* (1788), mechanics had undergone a meaningful generalisation, and an abstract physical space came to replace the ordinary Euclidean space in the tradition of mathematical physics. In the 1830s William Rowan Hamilton propounded a very abstract mechanics based on a set of variational principles expressed in generalised coordinates. In 1839, an Irish mathematician and natural philosopher, James MacCullagh, developed a mathematical theory of optics by Lagranginan methods. Another Irish physicist, George Francis FitzGerald, formulated a Lagrangian theory of electromagnetic fields in 1880[1].

Thermodynamics offered not only new technological improvements but also new theoretical horizons: the widespread philosophical and cosmological debate on the second law, the development of thermochemistry, and a new mathematization of an enlarged physics[2]. Different theoretical pathways were taken by physicists, even though we can single out two main traditions. James Clerk Maxwell and Ludwig Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, whereas other scientists relied on a macroscopic approach in term of continuous variables, setting aside specific mechanical models. One of the essential features of thermodynamics, the irreversibility of its laws regarding the inversion of time, made it very different from mechanics. The kinetic theory of Maxwell and Boltzmann nevertheless bridged the gap between the mechanical and thermal domains. Toward the end of the century, it was successfully applied to other fields including electromagnetism and radiation [Darrigol and Renn 2003, pp. 498 and 505; Boltzmann 1872, 1877; Maxwell 1860, 1867].

The purpose of this paper is to analyse the more abstract, potential-based approach to thermodynamics, its roots in Rudolf Clausius's and William Macquorn Rankine's researches in the mid-nineteenth century, the important developments that took place in the 1870s and 1880s, and lastly Pierre Duhem's construction of a very general theory that stemmed from the formal unification of mechanics and thermodynamics. From the outset I would like to highlight one of the hallmarks of that tradition of research: the assumption of a new *physical space*, where thermal variables (and variables of other kind) went along with time and geometrical variables in order to describe complex physical events. Different "mechanical theories of heat" were on stage in the last decades of the nineteenth century, and different meanings of the adjective *mechanical* were at stake.

A more detailed analysis would reveal nuances and different theoretical streams in the simplified picture of two traditions of research in the field of thermodynamics. A finer classification would require at least five streams, which can be sorted according to their conceptual distance from mechanics:

1. a purely phenomenological approach, where thermodynamics relied on its own foundations;

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[1] For the primary sources, cf. Hamilton 1834, MacCullagh 1848 (read 9 Dec. 1839), and FitzGerald 1880. On Hamilton's equations see Hankins 1980, pp. xv-xviii, 61-87, and 172-209. On MacCullagh's Lagrangian approach to Optics, and "Fitzgerald's electromagnetic interpretation of MacCullagh's ether", see Darrigol 2010, pp. 145-54, and 157-9.

[2] For the methodological and philosophical debate which stemmed from the second principle of thermodynamics, see Kragh 2008a, chapters 3 and 4.

2. the energetist approach, where thermodynamics emerged as a specific implementation of a science of energy;
3. a macroscopic approach based on structural analogy with abstract mechanics;
4. the combination of macroscopic and microscopic approaches based on the same analogy;
5. a microscopic approach, where specific mechanical models of forces and/or collisions merged with statistical assumptions that did not belong to the tradition of mechanics.

In this classification, the tradition under examination in the present study would correspond to the third item. However, even this refined historiographical framework might not be completely satisfactory. At least two clarifications are in order.

a) The researches that some scientists undertook in different stages of their career or even simultaneously could be associated with more than one theoretical stream. For instance, Planck contributed to the first and third theoretical stream, Helmholtz developed the third and the fourth, and J.J. Thomson was at ease along the third, fourth, and fifth.
b) Different nuances, and sometimes very different points of view, can be found within every theoretical stream. Regarding energetism, Helm's approach, which stemmed from the tradition of mathematical physics, was different from Ostwald's approach, which emerged in the context of the recently professionalized physical chemistry. Regarding statistical thermodynamics, not only can we find the original kinetic theory but also a more abstract approach in Boltzmann's memoirs of 1868 and 1871.

For the sake of the present study, the fourth stream deserves a few remarks for it somehow bridges the two main traditions with which I am dealing. Historians have already pointed out that Helmholtz's attempted to give a microscopic representation of heat, but without any recourse to specific mechanical models. In 1884, in the memoir entitled "Principien der Statik monocyklischer Systeme", he followed an intermediate pathway, which was neither Boltzmann's nor the Massieu-Gibbs pathway. 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. In 1888, Joseph John Thomson put forward a very general approach to physical and chemical problems. He remarked that physicists had at their disposal two different methods: a detailed mechanical description of the physical system, and a more general description that depended on "the properties of a single function of quantities fixing the state of the system". He acknowledged that he second approach, which was based on "purely dynamical principles", had already been "enunciated by M. Massieu and Prof. Willard Gibbs for thermodynamic phenomena". It is worth mentioning that the separation between mechanical and dynamical approaches had already been discussed in the context of the British theories of elasticity, in particular in 1845 by George Gabriel Stokes. As Norton Wise pointed out, "[Stokes] worked only with observable macroscopic concepts", and distinguished between "mechanical" and "dynamical" theories. He reserved the term mechanical theory for "speculations" into the structure of matter or aether, and dynamical theory for an approach independent of such hypotheses [Darrigol 2002, p. 142; Norton Wise 1982, pp. 185-6; Thomson 1888, pp. v-vi, 1-2, and 4; Stokes 1883, pp. 244-5]. When Thomson extended the dynamical method to those cases "in which we have to consider the effects of temperature upon the properties of bodies", he mentioned "a dynamical conception of temperature" that corresponded to "the Kinetic Theory of Gases": temperature was a measure of “the mean energy due to the translatory motion of the molecules of the gas”. Thomson here attributed two different meaning to the adjective “dynamical” at the risk of misleading his British readers. He in fact promoted the integration of dynamical methods and mechanical models. In his version of the Lagrangian approach, there were two kinds of coordinates: “controllable coordinates” on which macroscopic kinetic and potential energy depended, and “unconstrainable coordinates” on which microscopic kinetic energy [Thomson 1888, pp. 89-90].

1 The roots of a formal analogy

In 1854, Rudolf Clausius, who was then teaching at the Royal Artillery and Engineering School in Berlin, stated that the equivalence between heat and work, and “Carnot’s proposition” did not necessarily clash, provided that the latter was slightly modified. To the above law of equivalence he associated another law of equivalence, in order to maintain a sort of symmetry in the axiomatic structure of thermodynamics: a law of equivalence between “transformations”. He specified that two kinds of transformations were at stake in thermal machines: the transformation of heat into work, and the transformation of an amount of heat, which was stored in the boiler at a high temperature, into heat which is received by the cooler at a low temperature. Clausius pointed out that the two kinds of transformation were tightly linked to each other: the former could not take place without the latter [Clausius 1854, p. 133].

Clausius’s 1854 memoir consisted of a short introduction and two sections. The first was devoted to the first Principle, and its title was “Law of equivalence between heat and work”; the second, whose title was “Law of equivalence among transformations”, dealt with the second Principle. This formulation of the second law, pivoted on the concept of “equivalence value” Q/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” [Clausius 1854, p. 143].

Clausius counted positively the transformation of work into heat, as well as the transfer of heat from a high to a low temperature. In the case of n sources at the temperatures $T_1, T_2, \ldots, T_n$, he assumed that the quantities $Q_1, Q_2, \ldots, Q_n$ of exchanged heat were positive when received, and negative when sent off. Then he defined a quantity N as the sum of all “transformation values”

$$N = \sum \frac{Q}{T}.$$

In general, when temperatures changed continuously in the course of the transformation, the sum had to be replaced by the integral

$$N = \int \frac{dQ}{T}.$$

In the case of “reversible cyclic processes”, the sum or the integral vanishes ($\oint dQ/T = 0$) [Clausius 1854, pp. 140, 144-5, and 147][3].

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 transformation content, and the above integral became

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[3] In subsequent memoirs Clausius reversed the algebraic signs.

positive: the initial conditions could not be restored, and the transformation was "uncompensated".

> Now we will take into account non-reversible cyclic processes. [...] *The algebraic sum of all existing transformations can only be positive.* We will briefly label non-compensated transformation that kind of transformations which remains without any counterpart at the end of a cyclic process, and which can only be positive in accordance with our assumption[4].

In 1855 Clausius became Professor of mathematical physics at the Zurich Polytechnic. In 1862 he tried to deepen his 1854 approach, and in 1865 he put forward a theoretical synthesis which soon became well known. In the case of reversible transformations, the quantity dQ/T was "the complete differential" of a new physical entity S,

$$dS = \frac{dQ}{T},$$

whereas, in the case of irreversible transformations, the quantity dQ/T could be split into two terms,

$$\frac{dQ}{T} = \frac{dH}{T} + dZ,$$

which he had already introduced in 1862. The term dH corresponded to "the actually available heat in the body", which depended only on its temperature: in particular, dH did not depend on "the arrangement of its parts". The first term dH/T was a complete differential, and the second term Z was the "disgregation" in 1862: it depended on the "arrangement of the parts of the body," and its increase corresponded to "the transformation of work into heat" [Clausius 1865, pp. 31-3][5].

Clausius reported that he had been looking for a new word for the entity S, a word that would encapsulate the conceptual analogy between the "content of transformation" and the energy U. He chose the word "Entropie" as a German transliteration of the Greek "$\varepsilon\nu\tau\rho o\pi\eta'$", whose semantic field contains the meanings of transformation and conversion. He stressed that energy was the sum of two components: "the content of heat and the content of work"; in the same way, the "entropy" S was in general the sum of two components: the transformation value and the disgregation. He had "intentionally" looked for a word "as similar as possible to the word energy": the "physical meanings" of the two words "Energie" and "Entropie" were "so tightly related to each other that a certain linguistic similarity" had appeared to him particularly "convenient". The formal analogy between the first and second laws of thermodynamics, which he had put forward in 1854, was once more on the stage. According to Clausius, six physical entities were at the basis of "the mechanical theory of heat": "the content of heat", "the content of work", their sum, namely "the energy", "the value of transformation of the content of heat", "the disgregation", and their sum, namely "the entropy" [Clausius 1865, pp. 34-5].

Clausius's "theory of heat" was "mechanical" in a structural sense: the analogy between mechanics and the science of heat was an analogy between the corresponding laws. The adjective "mechanical" made reference to formal structures rather than specific mechanical models of heat. However, in the last part of his paper, he put forward a remarkable cosmological synthesis: the formal symmetry between energy

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[4] Clausius 1854, pp. 151-2.

[5] The word "Disgregation" did not appear in the monumental dictionary of German language the Grimm brothers were developing in the same years.

and entropy was partially broken, and the two laws became fundamental properties of the world as a whole. The following statements are well known:

1) Die Energie der Welt ist constant.
2) Die Entropie der Welt strebt einem Maximum zu[6].

Although British physicists initially criticised and misunderstood Clausius's entropy, in the long run scientists and philosophers came to grips with the word "entropy" and the concept of entropy increase. They entered scientific, philosophical, and theological debates, whereas "Verwandlungsinhalt" and "Disgregation" faded into the background. Nevertheless, Clausius's 1854 approach had the advantage of letting two structural analogies emerge: the structural analogy between the second and the first principle as two principles of equivalence, and the structural analogy between the second principle and the principle of conservation of mechanical energy. Mechanical energy was conserved in *pure* mechanical processes without dissipation, in the same way as the "Verwandlungsinhalt" was conserved in ideal thermodynamic processes without dissipation. In the 1870s Clausius's concept of disgregation was criticized by contemporary physicists, in particular Peter Guthrie Tait and Maxwell, but Gibbs reinterpreted it in terms of microscopic potential energy. Historians have noted that Clausius preferred to express the physical meaning of the second law in terms of this concept, and that he "had considered disgregation … a concept of greater physical significance than entropy", even though he "carefully omitted any mention" of it in the second edition of his 1876 book on thermodynamics [Deltete 2012, p. 123; Daub 1970, pp. 330-8; Klein 1969, pp. 129 and 139-44; Gibbs 1889; Maxwell 1878; Tait 1877].

The tradition of mechanics also offered structural analogies to the Scottish engineer Rankine. In 1855, when he was appointed to the chair of Engineering at Glasgow University, a position he maintained until his death, he had already made meaningful researches in the field of "pure science," in particular in the emerging thermodynamics. In the same year he published a wide-scope memoir, "Outline of the Science of Energetics" in the *Proceedings* of the Philosophical Society of Glasgow [Tait 1880, p. xxii]. According to Rankine, the whole of physics could be unified by the generalisation of the concepts of "*Substance*", "*Mass*", "*Work*", and energy. He insisted that such terms had to be looked upon as "purely abstract" or as "names" which made reference to "very comprehensive classes of objects and phenomena", rather than associated to "any particular object" or "any particular phenomena". He attained a further generalisation by introducing the terms *Accident* and *Effort*. If the former could be identified with "every variable state of substances", the latter was a generalisation of the concepts of force and pressure. The concept of *Passive Accident* was not fundamentally different from the concept of accident, apart from the further qualification of "condition which an effort tends to vary". It had to be distinguished by the concept of *Complex Accident*, which corresponded to "the whole condition or state of a substance": for instance, "thermic condition of an elastic fluid", and "condition of strain … in an elastic solid" were complex accidents for they required more than one independent variable (accident) to be specified [Rankine 1855, pp. 214-6].

The concept of work encompassed *accidents* and *efforts*, and was a key concept in Rankine's theory. The new meaning of the word "work" stemmed from the generalisation of the meaning of the words *force* and *displacement*, which corresponded to the new words *effort* and *accident*. The generalisation of the concept of work entailed the generalisation of the concept of energy, which was the core of Rankine's *Energetics*. The concept of "*Actual energy*" was a generalisation of the mechanical *living force*: it included "heat, light, electric current", and so on. The concept of "*Potential*

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[6] Clausius 1865, p. 44: "The energy of the universe is constant. The entropy of the universe tends to a maximum".

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 "the variation of any number of independent accident, each by the corresponding effect":

$$W = Xdx + Ydy + Zdz + \dots$$

[Rankine 1855, pp. 216-7 and 222].

Rankine's theoretical design required the re-interpretation of thermodynamic transformations in terms of transformations of actual energy, and then a further generalisation, in order to extend that reinterpretation to all physical sciences[7].

From the outset, explicit meta-theoretical commitments emerge from Rankine's paper. He distinguished between two kinds of scientific practice: the "*abstractive*" and the "*hypothetical*". In the former, scientists confined themselves to a mathematical re-interpretation and classification of physical phenomena; in the latter, they relied on models and analogies, in order to catch the intimate nature of phenomena or the hidden structures underlying them.

> According to the *abstractive* method, a class of object or phenomena is defined by describing, or otherwise making to be understood, and assigning a name or symbol to, that assemblage of properties which is common to all the objects or phenomena composing the class, as perceived by the senses, without introducing anything hypothetical. According to the *hypothetical* method, a class of object or phenomena is defined, according to a conjectural conception of their nature, as being constituted, in a manner not apparent to the senses, by a modification of some other class of objects or phenomena whose laws are already known. Should the consequences of such a hypothetical definition be found to be in accordance with the results of observation and experiment, it serves as the means of deducing the laws of one class of objects or phenomena from those of another[8].

Obviously, Rankine's reference to the possibility of practising science without making recourse to "anything hypothetical" is not consistent with whatever kind of actual scientific practice: it seems more an idealisation or a rhetorical contrivance than an actually pursued design. Nevertheless, the distinction put forward by Rankine was not meaningless, and his energetics was a sort of mathematical phenomenology interconnected with a strong commitment to theoretical unification. In reality, he did not disdain mechanical models: in 1851 he had devoted a paper to the relationship between heat and centrifugal forces arising from microscopic vortices. In 1853, in the paper "On the Mechanical Action of Heat – Section VI", he had discussed the "supposition" of "molecular vortices", the hypothesis that "heat consists in the revolutions of what are called molecular vortices", and he had more specifically assumed that "the elasticity arising from heat is in fact centrifugal force" [Rankine 1855, pp. 210 and 213, and Rankine 1853a, p. 310][9].

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[7] In his 1855 paper, the passages wherein he displayed his ambitious design are extremely synthetic. If we want to understand and appreciate the complex network of assumptions and derivations, we should first take a look at two papers he had read before the Philosophical Society of Glasgow in January 1853 ("On the Mechanical Action of Heat" and "On the General Law of the Transformation of Energy"), and then return to his 1855 paper.

[8] Rankine 1855, p. 210.

[9] In his 1851 paper, he reminded the reader about a specific atomic model he had already outlined the year before. See Rankine 1851, p. 49. It is worth noting that the distinction between *abstractive* and *hypothetical* theories was rephrased at the end of the century, in the context of the emerging theoretical physics.

2 A family of potentials

Fourteen years after Rankine's 1855 memoir, the mining engineer and professor at Rennes University François Massieu took the path of a mathematical generalisation of thermodynamics. After having attended the *École Polytechnique* and then the *École des Mines*, he had received a doctorate in mathematics. In two short memoirs published in the *Comptes Rendus*, he tried to give thermodynamics the formal structure of a very general theory. The infinitesimal amount of heat dQ received by a body could produce three effects: "external work" of dilatation, "internal work", and an increase of body "sensible heat". The last two effects could not be identified separately. From the mathematical point of view, at the microscopic level, a single function U accounted for the sum of "mechanical and thermal effects, which merge with each other", in accordance with the principle of equivalence between heat and work". The external work pdv was "thermally equivalent" to $Apdv$, wherein A was the well-known conversion factor between mechanical and thermal measures. The first principle could therefore be expressed by the equation

$$dQ = dU + Apdv.$$

If T was the "absolute temperature" ($T = t + 273$), at the end of a "closed reversible cycle", the result

$$\int \frac{dQ}{T} = 0$$

followed from "Joule and Carnot combined principles". Therefore dQ/T was "the exact differential dS of a function S of the variables which are sufficient to define the state of the body" [Massieu 1869a, p. 858].

After having chosen v and t (volume and temperature) as independent variables, and after some computations, he arrived at a function ψ whose differential

$$d\psi = \frac{U}{T^2}dt + \frac{Ap}{T}dv$$

was an exact differential of the same variables. Massieu labelled "*characteristic function of the body*" the function ψ. The most important mathematical and physical step consisted in deriving "all body properties dealing with thermodynamics" from ψ and its derivatives. Not only could U and S be expressed in terms of the function ψ, but also ψ could be expressed in terms of U and S:

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

[Massieu 1869a, p. 859, and Massieu 1869b, p. 1058][10].

Then Massieu introduced a second *characteristic function* ψ' in terms of the two variables t and p. He first defined a new function $U' = U + Apv$, and then put into operation the already mentioned and quite demanding mathematical engine. In the end,

$$U' = T^2\frac{\partial\psi'}{\partial t} \quad \text{and} \quad S = \psi' + T\frac{\partial\psi'}{\partial t}, \quad \text{or} \quad S = \frac{\partial}{\partial t}(T\psi') \quad \text{and} \quad \psi' = S - \frac{U'}{T}.$$

In the case of ideal gases,

$$\frac{U'}{T} = \frac{U}{T} + \frac{Apv}{T} = \frac{U}{T} + \text{const.},$$

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[10] In this context, mathematicians and physicists make reference to Legendre's transformations, but Massieu did not mentioned them.

and ψ and ψ' resulted the same function, apart from a constant value [Massieu 1869b, pp. 1059-60].

Massieu showed that not only could U, p, v, Q and S be derived from ψ and ψ', but also the specific heats at constant pressure or volume k and k', and the coefficient of dilatation at constant pressure or volume β and β' could as well. Conversely he was able to give the specific mathematical expressions of ψ and ψ' in terms of T, v, p, and the specific heats k and k', for ideal gases, saturated vapours and superheated vapours [Massieu 1869b, pp. 1060-1].

After seven years, in an essay of almost one hundred pages published in the *Mémoires présentés par divers savants à l'Académie des Sciences de l'Institut National de France*, he resumed the subject matter, and generalised and deepened his theoretical approach. Indeed, compared with the previous short paper, the essay had a wider scope, and exhibited an explicit meta-theoretical commitment. At first, he regretted "the poor connections among the different properties of bodies, and among the general laws of physics". Nevertheless, according to Massieu, this gap had begun to be filled just by the unifying power of thermodynamics, which he identified with "the mechanical theory of heat".

> With regard to the mechanical and thermal properties of a body, thermodynamics or the mechanical theory of heat has bridged the gap. Relations that had not yet managed to find a clear and really scientific expression can now be derived from the two general principles on which this new science is based[11].

It is worth remarking that, in Massieu's theoretical and meta-theoretical context, "mechanical" did not mean microscopic mechanical models in the sense of Maxwell and Boltzmann, but a mathematical approach on the track of analytical mechanics. 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 [Massieu 1876, pp. 2-3].

In this 1876 essay, the deduction of the characteristic function is shorter than in the previous paper. From $dS = dQ/T$ and $dQ = dU + Apdv$, we obtain $TdS = dU + Apdv$. The addition of the term $Sdt = SdT$ to both members yielded

$$TdS + SdT = dU + Apdv + SdT,$$

$$d(ST) = dU + Apdv + SdT,$$

$$d(ST - U) = Apdv + SdT.$$

Since the first member was an exact differential, so was the second, and Massieu could write

$$dH = d(ST - U), \quad H = ST - U,$$

where the function H corresponded to the function ψ of the previous paper. Moreover

$$S = \frac{dH}{dt}, \quad Ap = \frac{dH}{dv}, \quad U = ST - H \quad \text{or} \quad U = T\frac{dH}{dt} - H$$

[Massieu 1876, pp. 9-10].

The choice of t and p instead of t and v as independent variables led to Massieu's second characteristic function H', which corresponded to the function ψ' of the previous paper. A two-fold strategy, both mathematical and physical, was at stake. On

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[11] Massieu 1876, p. 2.

the one hand, the knowledge of specific parameters and specific laws describing the physical system under consideration allowed the researcher to write explicit expression for U', Q and S, and then H'. On the other hand, all parameters and specific equations describing the specific system could be derived from the knowledge of H': in Massieu's words, after having put the mathematical engine into operation, "it is only a matter of computation" [Massieu 1876, pp. 29 and 43].

An abstract approach and wide-scope generalisations were also the hallmarks of Josiah Willard Gibbs's researches on thermodynamics. He was an American engineer who had accomplished his scientific training in Paris, Berlin and Heidelberg: after having been appointed to the chair of mathematical physics at Yale in 1871, he published a series of fundamental papers under the common title "On the equilibrium of heterogeneous substances" in the *Transactions of the Connecticut Academy* in the years 1875-78. In the first lines of his collection of papers, Gibbs stated that his theoretical approach was based on the two fundamental principles of thermodynamics, which had been put forward by Clausius in 1865. Starting from two basic entities, energy and entropy, he would have set up "the laws which govern any material system": energy and entropy's "varying values" would "characterize in all that is essential" the transformations of every system. His theoretical physics dealt with a "thermodynamic system", because "all material systems" could be looked upon as such, and thermodynamics could be looked upon as a generalisation of ordinary mechanics. In the building up of his general theory, he followed the analogy with "theoretical mechanics", which took into account "simply mechanical systems . . . which are capable of only one kind of action", namely "the performance of mechanical work". In this specific case, there was a function "which expresses the capability of the system for this kind of action", and the condition of equilibrium required that "the variation of this function shall vanish". In his more general mechanics, there were two functions corresponding to "the twofold capability of the system". According to Gibbs, every material system "is capable of two different kinds of action upon external systems", and the two functions "afford an almost equally simple criterion of equilibrium" [Gibbs 1875-8, pp. 55-6].

Immediately he put forward two complementary criteria of equilibrium for isolated systems, the first under the condition of a constant energy ε, and the second under the condition of a constant entropy η.

> I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative . . . the condition of equilibrium may be written
> $$(\delta\eta)_\varepsilon \leqslant 0.$$
>
> II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive. This condition may be written
> $$(\delta\varepsilon)_\eta \geqslant 0$$[12].

In other words, in transformations taking place at constant energy, the equilibrium corresponded to the maximum entropy, whereas in transformations taking place at constant entropy, the equilibrium corresponded to the minimum energy. As a first application, he considered "a mass of matter of various kinds enclosed in a rigid and fixed envelope", which was impermeable to both matter and heat fluxes. It was a very simplified case, wherein "Gravity, Electricity, Distorsion of the Solid Masses, or Capillary Tensions" were excluded [Gibbs 1875-8, p. 62].

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[12] Gibbs 1875-8, p. 56.

For every "homogeneous part of the given mass" Gibbs wrote down the equation

$$d\varepsilon = td\eta - pdv,$$

which was nothing else but the first principle of thermodynamics. The first term in the second member was "the heat received", and the second term "the work done"; v, t, and p were volume, temperature, and pressure. Since Gibbs was not confining himself to "simply mechanical systems", he let "the various substances $S_1, S_2, \ldots S_n$ of which the mass is composed" change their mass. As a consequence, the energy ε of the homogeneous component of the system could also depend on the corresponding variable masses m_1, m_2, $\ldots m_n$:

$$d\varepsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \ldots \mu_n dm_n,$$

where μ_1, μ_2, $\ldots \mu_n$ denoted "the differential coefficients of ε taken with respect to m_1, m_2, $\ldots m_\mathrm{n}$". In general, also "component substances which do not initially occur in the homogeneous mass considered" had to be taken into account. To the coefficients μ_x Gibbs attributed the qualification of "potential for the substance S_x" [Gibbs 1875-8, pp. 63-5].

In more complex systems, each homogeneous sub-set depended on the $(n + 2)$ variables $t, v, m_1, m_2, \ldots m_n$, and the whole system depended on $(n+2)\nu$, wherein ν was "the number of homogeneous parts into which the whole mass is divided". The series of equations involving t, p, and μ_1, μ_2, $\ldots \mu_n$ contained exactly $(\nu - 1)(n + 2)$ conditions among the $(n + 2)\nu$ variables. From the mathematical point of view, the remaining unknown variables were $(n + 2)$. If the volume of "the whole mass", and "the total quantities of the various substances" were known, then additional $(n + 1)$ conditions were available. Therefore only one unknown variable remained, but the knowledge of "the total energy of the given mass", or alternatively "its total entropy", led to "as many equations as there are independent variables" [Gibbs 1875-8, p. 66]. Alongside the algebraic problem, which Gibbs showed to be solvable, there was a very general physical problem: his general mathematical theory allowed him to derive the mechanical, thermal and chemical properties of a given physical system.

In the subsequent section, "Definition and Properties of Fundamental Equations", Gibbs put forward other "fundamental equations" for a thermodynamic system, which involved new thermodynamic functions. The adjective "fundamental" meant that "all its thermal, mechanical, and chemical properties" of the system could be derived from them. He defined three functions

$$\psi = \varepsilon - t\eta, \quad \chi = \varepsilon + pv, \quad \zeta = \varepsilon - t\eta + pv.$$

Under specific conditions, the functions ψ, χ, and ζ assumed specific meanings, and led to new conditions of equilibrium [Gibbs 1875-8, p. 89][13].

Gibbs was weaving the plot of a more general mechanics of equilibrium: he followed the track of analytical mechanics, but aimed at a wider-scope mechanics, which encompassed mechanics, thermodynamics and chemistry.

From the mathematical point of view, the fundamental functions ε, ψ, χ, and ζ were interchangeable: ε as a function of volume and entropy could be replaced by ψ as a function of temperature and volume, by χ as a function of entropy and pressure, or by ζ as a function of temperature and pressure. In brief, every fundamental function, associated to its two independent variables, defined a threefold system of co-ordinates,

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[13] 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* $G = U - TS + pV$ [Müller 2007, pp. 70, 131-2, and 147-8; Kragh and Weininger 1996, p. 99].

wherein the graph of the corresponding function $z = f(x, y)$ could be drawn: four functions $\varepsilon = f_\varepsilon(v, \eta)$, $\psi = f_\psi(v, t)$, $\chi = f_\chi(p, \eta)$, and $\zeta = f_\zeta(p, t)$ could be defined. We have in front of us a sort of symmetry, which transforms the space (v, η, ε) into the space(v, t, ψ), (p, η, χ), or (t, p, ζ) [Gibbs 1875-8, pp. 89, 93, and 116][14].

He did not try to describe complex thermodynamic systems by means of mechanical models: on the contrary, purely mechanical systems were looked upon as specific instances of thermodynamic ones. The relationship between mechanics and thermodynamics consisted of a formal analogy: the mathematical structure of mechanics offered a formal framework for the mathematical structure of thermodynamics.

The same view was confirmed in a subsequent abstract Gibbs published in the *American Journal of Science* in 1878. From the outset he stressed the role of entropy, whose importance did "not appear to have been duly appreciated": he claimed that "the general increase of entropy . . . in an isolated material system" would "naturally" suggest that the maximum of entropy be identified with "a state of equilibrium". He emphasised the role of the function ψ besides the functions ε and η, and the corresponding condition of equilibrium: when "the temperature of the system is uniform", the condition of equilibrium could "be expressed by the formula" $(\delta\psi)_t \geqslant 0$. This inequality seemed to Gibbs suitable for equilibrium in "a purely mechanical system", as a mechanical system was nothing else but "a thermodynamic system maintained at a constant temperature". In the conceptual "transition" from "ordinary mechanics" to thermodynamics, the functions -ε and -ψ could "be regarded as a kind of force-function", namely a generalisation of the concept of mechanical potential. The conditions of equilibrium $(\delta\varepsilon)_\eta \geqslant 0$ and $(\delta\psi)_t \geqslant 0$ would represent "extensions of the criterion employed in ordinary statics to the more general case of a thermodynamic system" [Gibbs 1875-8, pp. 354-5][15].

The role of entropy, the structural analogy between thermodynamics and analytical mechanics, and a unifying theoretical framework for physics and chemistry were also the main features of Helmholtz's pathway to thermodynamics. At the beginning of the 1880s, he was a scientific authority: it is worth stressing that, in the scientific community of the time, he played a role quite different from Massieu, Rankine and Gibbs. After an academic career as a physiologist at Königsberg and Heidelberg universities, he had been appointed professor of physics at Berlin university in 1871, and then rector for the academic year 1877-8. He had delivered scientific lectures in many German universities and even in English universities and institutions, not to mention the honours received from French and English institutions. After having made important contributions to physics and physiology, in 1882 Helmholtz put forward a mathematical theory of heat pivoted on the concept of "free energy"[16].

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[14] See, in particular p. 93: "In the above definition we may evidently substitute for entropy, volume, and energy, respectively, either temperature, volume, and the function ψ; or entropy, pressure, and the function χ; or temperature, pressure, and the function ζ".

[15] As remarked by Truesdell in the second half of the twentieth century, Gibbs built up a remarkable "axiomatic structure", but his theory was "no longer the theory of motion and heat interacting, no longer thermodynamics, but only the beginnings of thermostatics" [Truesdell 1984, p. 20]. The same concept is re-stated in Truesdell 1986, p. 104. Nevertheless Truesdell appreciated Gibbs's stress on entropy. See Truesdell 1984, p. 26: "While he made his choice of entropy and absolute temperature as primitive concepts because that led to the most compact, mathematically efficient formulation of special problems as well as of the structure of his theory, of course he knew that entropy was not something obvious, not something that comes spontaneously to the burnt child who is learning to avoid the fire".

[16] For a brief scientific biography, see Cahan 1993b, p. 3. For a general account of Helmholtz's contributions to thermodynamics and Thermo-Chemistry, see Bierhalter 1993, and Kragh 1993.

From the outset he put forward a unified theoretical approach for physical and chemical processes, based on the two principles of thermodynamics. In particular, he found that thermo-chemical processes, in particular the production or dissolutions of chemical compounds, could not be interpreted in terms of mere production or consumption of heat. A more satisfactory theory had to take into account the fact that an amount of heat was not indefinitely convertible into an equivalent amount of work, according to Clausius's interpretation of the Carnot law. It is worth remarking that, since the 1860s, Thermo-Chemistry "rested on the Thomsen-Berthelot principle" or "principle of maximum work", which relied only on the energy involved in chemical transformations. According to that principle, chemical reactions "were accompanied by heat production", and in these processes "the most heat was produced". In this "classical thermo-chemistry" the second principle of thermodynamics had been underestimated, and entropy appeared as an obscure and unfruitful concept. In the same years, Helmholtz himself and W. Thomson had put forward the "general idea that in a galvanic cell chemical energy was completely transformed into electric energy". Helmholtz realized that the second Principle of thermodynamics required a reassessment of his previous point of view [Kragh and Weininger 1996, pp. 94-5; Kragh 1993, pp. 404 and 409; Helmholtz 1882, pp. 958-9].

Historians have pointed out the close relationship between the emergence of physical chemistry and the application of thermodynamics to chemistry: the concept of entropy played an important role in that process. Gibbs and Helmholtz corrected the simplified law, which could successfully be applied only at low temperatures: Gibbs was the first to use the concept of entropy in a systematic and original way in the context of chemistry. Nevertheless the founding fathers of physical chemistry, Jacobus Henricus van 't Hoff, Svante Arrhenius, and Wilhelm Ostwald found Gibbs's approach too abstract. In particular, van 't Hoff did not make use of the concept of entropy, neither in his famous 1884 dissertation nor in his 1898-1900 huge treatise on physical chemistry. As John W. Servos remarked in 1990, "thermodynamics was largely in the hands of physicists", and when physicists began to apply thermodynamics to chemistry in the 1870s, "their results were, for the most part, ignored by chemists". Gibbs had developed "a system of chemical thermodynamics that was very nearly complete", but "Gibbs's style was that of a theoretical physicist: concise, mathematical, and abstract". As a consequence, "Gibbs's ideas had negligible influence on chemistry until after 1890, and even then his work was cited more often than it was studied" [Müller 2007, p. 155; Kragh and Weininger 1996, pp. 92, 98, and 102; Servos 1990, pp. 18-20].

Nevertheless the historical landscape was not so sharply one-sided, as historians themselves have pointed out. In 1892, Ostwald translated Gibbs's work into German, and in 1899 Henri Louis Le Chatelier translated it into French. Those translations contributed to make Gibbs known, and his theoretical approach came to be appreciated: in 1901 he received the Copley medal of the Royal Society of London. Moreover as early as 1864, the Dutch scientist Schröder van der Kolk had made use of the second law of thermodynamics in the context of chemistry, and then August Horstmann had made use of Clausius's concept of disgregation in 1869 and 1873 [Müller 2007, pp. 128-9; Kragh and Weininger 1996, pp. 96-7].

Helmholtz labelled 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 Clausius had introduced "two functions of temperature and another parameter, which he called the Energy U and the Entropy S", Helmholtz showed that "both of them can be expressed as differential quotients of a completely defined Ergal" or thermodynamic potential. If P_α was the external force corresponding to the coordinate p_α, and $P_\alpha \cdot dp_\alpha$ the corresponding work, then the total external work was

$dW = \sum_{\alpha} (P_\alpha \cdot dp_\alpha)$. According to the first principle,

$$\mathrm{J} \cdot dQ = dU + \sum_{\alpha} (P_\alpha \cdot dp_\alpha),$$
$$\mathrm{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \sum_{\alpha} \left(\frac{\partial U}{\partial p_\alpha} \cdot dp_\alpha \right) + \sum_{\alpha} (P_\alpha \cdot dp_\alpha).$$

Here J is the mechanical equivalent of the heat unit, and $P_\alpha \cdot dp_\alpha$ the freely convertible work corresponding to the variation dp_α. It can either be conveyed to the surrounding bodies or transformed into the living force of the system. The latter could also be looked upon as an external work which opposes the internal modifications of the system[17].

Beside this generalisation of the first principle, Helmholtz put forward a similar generalisation of the second law. He defined the entropy S as dQ/ϑ, or more specifically

$$dS = \frac{\partial S}{\partial \vartheta} \cdot d\vartheta + \sum_{\alpha} \left[\frac{\partial S}{\partial p_\alpha} \cdot dp_\alpha \right].$$

Then he derived an equivalent expression from the first Principle:

$$\mathrm{J} \cdot \frac{dQ}{\vartheta} = \frac{1}{\vartheta} \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \frac{1}{\vartheta} \sum_{\alpha} \left[\left(\frac{\partial U}{\partial p_\alpha} + P_\alpha \right) \cdot dp_\alpha \right],$$

and the physical equivalence led to the mathematical relations

$$\mathrm{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \mathrm{J} \cdot \frac{\partial S}{\partial p_\alpha} = \frac{1}{\vartheta} \cdot \left(\frac{\partial U}{\partial p_\alpha} + P_\alpha \right)$$

[Helmholtz 1882, p. 967].

From the second equation, a simple and interesting expression for generalised forces followed:

$$\mathrm{J} \cdot \vartheta \cdot \frac{\partial S}{\partial p_\alpha} = \frac{\partial U}{\partial p_\alpha} + P_\alpha \quad \text{or} \quad P_\alpha = \frac{\partial}{\partial p_\alpha} \cdot (\mathrm{J} \cdot \vartheta \cdot S - U).$$

The function $\mathrm{F} = U - \mathrm{J} \cdot \vartheta \cdot S$ played the role of a generalised potential for the forces P_α:

$$P_\alpha = -\frac{\partial \mathrm{F}}{\partial p_\alpha}.$$

According to Helmholtz, the function F represented the potential energy or the "Ergal" in the thermodynamic context. The functions U and S could be derived from F by simple derivation:

$$\frac{\partial \mathrm{F}}{\partial \vartheta} = -\mathrm{J} \cdot S, \quad \text{and} \quad U = \mathrm{F} + \mathrm{J} \cdot \vartheta \cdot S \quad \text{or} \quad U = \mathrm{F} - \vartheta \cdot \frac{\partial \mathrm{F}}{\partial \vartheta}$$

[Helmholtz 1882, pp. 968-9][18].

The function F also represented the "free energy", namely the component of the internal energy which could be transformed into every kind of work. If U represented

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[17] Helmholtz 1882, pp. 966-7.

[18] Helmholtz did not seem aware of Massieu's result, which had probably not crossed the France borderlines. Clausius had already coined the terms "ergal" and "ergon" in order to represent "the force function" and work [Daub 1970, p. 332, fn 56].

the total internal energy, the difference between U and F, namely $\mathrm{J} \cdot \vartheta \cdot S$, represented the "bound energy", namely the energy stored in the system as a sort of *entropic* heat [Helmholtz 1882, p. 971].

In the second section of his paper, Hemholtz tried to re-interpret "the other two quantities dW and dQ which appears in Clausius's equations". For this purpose he found it necessary to introduce two differential operators: he labelled δ the variation of whatever function φ when the parameters p_α changed but the temperature did not, whereas the symbol d corresponded to a complete variation, when the temperature also changed. For a function φ of p_α and ϑ,

$$\delta\varphi = \sum_\alpha \left(\frac{\partial\varphi}{\partial p_\alpha} dp_\alpha \right) \quad \text{and} \quad d\varphi = \delta\varphi + \frac{\partial\varphi}{\partial\vartheta} d\vartheta.$$

The external work or what he called "freely convertible external work" dW could be expressed in term of the new derivatives. Since $P_\alpha = -\partial F/\partial p_\alpha$,

$$dW = \sum (P_\alpha \cdot dp_\alpha) = \sum \left(-\frac{\partial \mathrm{F}}{\partial p} \cdot dp_\alpha \right) = -\delta \mathrm{F}$$

[Helmholtz 1882, pp. 972-3].

According to the new symbols, the first principle assumed the form

$$\mathrm{J} \cdot dQ = dU - \delta \mathrm{F}.$$

The free energy represented only a part of the total energy U: the remaining part was labelled "bound energy" or "bound work" or G. From the mathematical point of view, $\mathrm{F} + \mathrm{G} = U$. Helmholtz offered a mathematical and conceptual alternative to the first principle expressed in terms of W and Q: $\mathrm{F} + \mathrm{G} = U$ instead of $\mathrm{J} \cdot dQ = dU + dW$.

Here Helmholtz's *mechanical* approach to thermodynamics is in accordance with the tradition of analytical mechanics. In the subsequent years, he tried to follow a slightly different pathway, wherein some hypotheses on the mechanical *nature* of heat were put forward, as I have already pointed out in the Introduction.

3 Physical and mathematical symmetries

In the meantime, in 1880, the young German physicist Max Planck was pursuing a slightly different aim. He lamented that the theory of mechanical processes, in particular mechanical 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. In the dissertation *Gleichgewichtzustände isotroper Körper in verschiedenen Temperaturen*, which he published in order to be given the *venia legendi*, he outlined a mathematical theory where the mechanics of continuous media merged with thermal processes. Planck became *Privatdocent* at the University of Munich in 1880, and was appointed as extraordinary professor of physics at the University of Kiel in 1885. In 1889, two years after Kirchhoff's death, he became assistant professor at the University of Berlin, and director of the Institute for Theoretical physics: in 1892 he was appointed ordinary professor [McCormmach and Jungnickel 1986, vol. 2, pp. 51-2, 152, and 254; Gillispie (ed.), 1970-80, volume XI, p. 8].

He relied on the two principles of "the mechanical theory of heat", and "specific assumptions on the molecular structure [Beschaffenheit] of bodies" were "not necessary". In accordance with this theoretical option, he assumed that isotropic bodies consisted of "*continuous* matter". The body could be subject to "an external pressure", and the condition of equilibrium was assured by the counteraction of "internal elastic forces". 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 $(v';T')$. In particular the geometrical co-ordinates of a point inside the body underwent a transformation in accordance with the equations

$$x = x_0 + \xi; \quad y = y_0 + \eta; \quad z = z_0 + \zeta,$$

where x_0, y_0, z_0 are the initial values and ξ, η, ζ the infinitesimal variation. The elastic forces acting on the surfaces parallel to the planes YZ, ZX, and XY were labelled by Planck $X = (X_x, X_y, X_z)$, $Y = (Y_x, Y_y, Y_z)$, and $Z = (Z_x, Z_y, Z_z)$, where $X_y = Y_x$, $Y_z = Z_y$, $Z_x = X_z$, "as usually assumed in the theory of elasticity" [Planck 1880, pp. 3-4][19].

In the internal part of the body, the conditions of equilibrium were

$$\begin{aligned}\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} &= 0,\\ \frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} &= 0,\\ \frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} &= 0,\end{aligned}$$

whereas on the external surface they were

$$\begin{aligned}\Xi + \alpha X_x + \beta X_y + \gamma X_z &= 0\\ \mathrm{H} + \alpha Y_x + \beta Y_y + \gamma Y_z &= 0\\ \mathrm{Z} + \alpha Z_x + \beta Z_y + \gamma Z_z &= 0,\end{aligned}$$

where $(\Xi, \mathrm{H}, \mathrm{Z})$ were the components of the external force, (α, β, γ) the directive cosines, and $d\Phi = \Xi \cdot d\xi + \mathrm{H} \cdot d\eta + \mathrm{Z} \cdot d\zeta$ the work done by the external force [Planck 1880, pp. 4-6][20].

The first principle of thermodynamics allowed a unified account of phenomena, and a unified overview on physical space. If $T' = T + \tau$ was the relationship between initial and final temperature in the course of a transformation, Planck specified that, in the end, energy depended on τ and on the derivative of (ξ, η, ζ) with reference to (x, y, z). In particular it depended on the seven new variables τ and Cauchy's six strain components,

$$\begin{gathered}x_x = \frac{\partial \xi}{\partial x}, \quad y_y = \frac{\partial \eta}{\partial y}, \quad z_z = \frac{\partial \zeta}{\partial z},\\ x_y + y_x = \frac{\partial \xi}{\partial y} + \frac{\partial \eta}{\partial x}, \quad y_z + z_y = \frac{\partial \eta}{\partial z} + \frac{\partial \zeta}{\partial y}, \quad z_x + x_z = \frac{\partial \zeta}{\partial x} + \frac{\partial \xi}{\partial z}\end{gathered}$$

[Planck 1880, pp. 9-10].

Cauchy had put forward a two-constant relation between stress and deformation, which is "the one now accepted for isotropic elasticity". In brief

$$\begin{gathered}\sigma_x = kx_x + K\theta, \quad \sigma_y = ky_y + K\theta, \quad \sigma_z = kz_z + K\theta,\\ \tau_{xy} = \frac{k}{2}\left(x_y + y_x\right), \quad \tau_{yz} = \frac{k}{2}(y_z + z_y), \quad \tau_{xz} = \frac{k}{2}(z_x + x_z)\end{gathered}$$

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[19] On the developments of the theory of elasticity in the first half of the XIX century, see Darrigol 2002, in particular sections from 2 to 6.

[20] He specified that elastic forces could not rely on "a potential", because "they depended on temperature" (p. 8).

where k and K are the two elastic constants, and $\theta = \varepsilon_x + \varepsilon_y + \varepsilon_z$ is the unit volume change.

In 1852 the mathematician and engineer Gabriel Lamé published the first book on the theory of elasticity, *Leçons sur la Théorie Mathématique de l'Élasticité des Corps Solides*. He came to the conclusion that "to determine the elastic properties of an isotropic material, two elastic constants were required." It is worth mentioning that thermo-elastic equations had already put forward by Duhamel in 1838, and Franz Neumann in 1841, quite before the emergence of thermodynamics [Darrigol 2002, pp. 119-20; Timoshenko 1983, pp. 107, 110, 116-7, and 242-3; Barus 1905, pp. 356].

After having simplified typographically "the dilatation of the unitary volume" by means of a new variable $\varTheta = (x_x + y_y + z_z)$, Planck chose an expression for the energy dU of "the element of mass dM" in terms of the new variables:

$$\begin{aligned} dU = dM[\text{const.} + k \cdot \tau + l \cdot \varTheta + \frac{m}{2} \cdot \tau^2 + p \cdot \tau\varTheta + \frac{q}{2} \cdot \varTheta^2 \\ + r \cdot \left(x_x^2 + y_y^2 + z_z^2\right) + \frac{r}{2}\left(x_y^2 + y_z^2 + z_x^2\right). \end{aligned}$$

The formal structure of entropy was not so different from that of energy:

$$\begin{aligned} dS = dM[\text{const.} + k' \cdot \tau + l' \cdot \varTheta + \frac{m'}{2} \cdot \tau^2 + p' \cdot \tau\varTheta + \frac{q'}{2} \cdot \varTheta^2 \\ + r' \cdot \left(x_x^2 + y_y^2 + z_z^2\right) + \frac{r'}{2}\left(x_y^2 + y_z^2 + z_x^2\right). \end{aligned}$$

Planck could compare the two expression and the two sets of coefficients by means of the relationship between energy and entropy:

$$dS = \frac{dQ}{T} = \frac{dU - d\varPhi}{T} \quad \text{[Planck 1880, pp. 12-6].}$$

The comparison gave rise to seven relationships between the derivatives of u and s, namely the densities of energy and entropy:

$$\begin{aligned} \frac{\partial u}{\partial \tau} &= T'\frac{\partial s}{\partial \tau}, \\ \frac{\partial u}{\partial x_x} + v'X_x &= T'\frac{\partial s}{\partial x_x}, \\ \frac{\partial u}{\partial y_y} + v'Y_y &= T'\frac{\partial s}{\partial y_y}, \\ \frac{\partial u}{\partial z_z} + v'Z_z &= T'\frac{\partial s}{\partial z_z}, \\ \frac{\partial u}{\partial x_y} + v'X_y &= T'\frac{\partial s}{\partial x_y}, \\ \frac{\partial u}{\partial y_z} + v'Y_z &= T'\frac{\partial s}{\partial y_z}, \\ \frac{\partial u}{\partial z_x} + v'Z_x &= T'\frac{\partial s}{\partial z_x}. \end{aligned}$$

The first relationship led to

$$k = Tk', \quad m = Tm' + k', \quad p = Tp'.$$

The second, third and fourth led to

$$X_x = \frac{Tl' - 1}{v} + \frac{l'}{v} \cdot \tau - \frac{(q-l) - T(q'-l')}{v} \cdot \Theta - \frac{2(r - Tr')}{v} \cdot x_x, \tag{1}$$

and similar expressions for Y_y and Z_z.

The fifth, sixth and seventh led to

$$X_y = -\frac{r - Tr'}{v} \cdot x_y, \tag{2}$$

and other similar expressions for Y_z and Z_x [Planck 1880, pp. 17-8].

The combinations of coefficients in (1) and (2) could be typographically simplified in accordance with simple physical remarks and the typographical tradition of the theory of elasticity. If the first expression in (1) corresponded to the external pressure, the third expression corresponded to the traditional term λ, whereas the fourth expression in (1) and that in (2) corresponded to the traditional term μ. In brief:

$$P = \frac{Tl' - 1}{v},$$
$$\lambda = \frac{(q-l) - T(q'-l')}{v},$$
$$\mu = \frac{r - Tr'}{v},$$

and therefore

$$X_x = P + \frac{l'}{v} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x,$$
$$X_y = -\mu \cdot x_y \text{ [Planck 1880, p. 19]}^{21}.$$

Internal energy, entropy, and the specific heats could be expressed in terms of k, λ, μ, and the other coefficient α, which represented "the variation of the specific volume with temperature, at constant pressure", namely

$$\alpha = \left(\frac{v' - v}{T' - T}\right)_P = v\left(\frac{\Theta}{\tau}\right)_P.$$

If

$$u = k \cdot \tau + \left[\alpha\left(\lambda + \frac{2}{3}\mu\right)T - Pv\right] \cdot \Theta \quad \text{and} \quad s = \frac{k}{T} \cdot \tau + \alpha\left(\lambda + \frac{2}{3}\mu\right) \cdot \Theta,$$

then the constant k could be identified with "the specific heat at constant volume". Planck showed that the specific heat at constant pressure could be expressed by

$$c = k + \alpha^2\left(\lambda + \frac{2}{3}\mu\right)\frac{T}{v}.$$

In the end,

$$X_x = P + \frac{\alpha(3\lambda + 2\mu)}{3v} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x \quad \text{[Planck 1880, pp. 21-3]}.$$

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[21] For the introduction of parameters λ and μ in the theory of elasticity in the first half of the nineteenth century, see Darrigol 2002, pp. 110, 113, and 122-4.

In brief, 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. In the remaining part of the chapter, Planck showed some applications to specific states of matter: solid bodies, fluid drops, and vapours and gases.

Two years later, in the paper "Vaporising, melting, and sublimating" ("Verdampfen, Schmelzen und Sublimiren"), he claimed once again that his theoretical approach was based on "the two principles of the mechanical theory of heat", and was "completely independent of any assumption on the internal structure of bodies". In physical-chemical transformations there were "several states corresponding to relative maxima of entropy", but there was only one "stable state of equilibrium", which corresponded to "the absolute maximum of entropy": the others states were nothing more than "unstable states of equilibrium". In the last part of his paper, Planck stressed that his previous statements were pure consequences of a more general law: "in natural processes, the sum of the entropies of the parts of a given body does increase". Only in reversible processes, the entropy would remain unchanged, but those kinds of processes did "not really exist": they could "be looked upon as merely ideal". When a physical system reached the maximum entropy, "no transformation" could "take place any more". The maximum entropy would therefore correspond to "a stable state of equilibrium", and this correspondence between entropy and equilibrium would represent "the best way to base the search for the conditions of equilibrium on rational grounds", both in physics and chemistry [Planck 1882, pp. 452 and 472][22].

Planck published a series of papers and essays on thermodynamics between 1880 and 1892. In 1879, in his doctoral thesis, he had stressed that the increase of entropy dealt with all natural processes: in no way was it confined to thermal phenomena. He held the same position on the foundation of thermodynamics for many years. In 1891, in a paper he read at the annual meeting of German scientists, Planck claimed that Maxwell and Boltzmann's skilful "analysis of molecular motion" was not "adequately rewarded by the fruitfulness of the results gained". In particular, he found that the kinetic theory was not at ease with phenomena placed on the borderline between physics and chemistry: he did not expect that it could "contribute to further progress" in that field. Similar remarks can be found in the book on the foundation of Thermochemistry Planck published in 1893. As Darrigol and Renn pointed out some years ago, "Helmholtz and Planck preferred a macroscopic approach in terms of differential equations, which involved really observable entities". Nevertheless they had different attitudes with regard to molecular hypotheses: whereas Helmholtz made minimal use of them without denying molecular reality, Planck rejected any form of atomism [Deltete 2012, pp. 3-4; Darrigol and Renn 2003, pp. 503 and 505; Kuhn 1987, p. 22; Born 1948, p. 163].

In 1885 the German speaking physicist Arthur von Oettingen, who held the chair of physics in Dorpat University (now Tartu, Estonia), undertook an even more ambitious design: a formal theory, where mechanical work and heat flows represented the starting point of a dual mathematical structure. A large family of thermal and mechanical "capacities" emerged. After having studied at Dorpat, in Livonia (now Tartu, Estonia), he had spent some years in Augustine Bequerel's and Henri Victor Régnault's laboratories in Paris, and then in Heinrich Gustav Magnus's, Johann Christian Poggendorff's and Heinrich Wilhelm Dove's laboratories in Berlin. In 1868 he became Professor of

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[22] The distinctive feature of an unstable equilibrium was the establishment of "a finite change of state" as a consequence of "an arbitrary small change in external conditions". According to Planck, a specific instance of unstable equilibrium was offered by "explosions in mixtures of gases", where the addition of "a convenient but arbitrary small amount of energy" could trigger off sudden and dramatic transformations (*Ibidem*, p. 474).

physics at Dorpat. In 1876 he had criticised Clausius's version of the second law because he thought that it did not imply that "a system will end in a state of maximum entropy, even if an infinity of time was available" [Kragh 2008, pp. 388 and 394 fn 38; Oettingen 1876].

His long essay was published in the *Mémoires de l'Académie impériale des sciences de Saint-Pétersbourg*, and its complete title was "Die thermodynamischen Beziehungen antithetisch entwickelt" (Antithetically developed thermodynamic connections). The German adjective and adverb "antithetisch" might be interpreted in two different ways: either the opposition to traditional approaches to thermodynamics, or the development of antithetical or complementary mathematical relations in the body of knowledge of thermodynamics. In some way, both interpretations are suitable, because both of them manage to catch the original content of the paper. From the outset the author stressed that the great number of "multifarious relations" in physics could be encompassed by "a unitary viewpoint", and could be "grouped and ordered in a rigorous system". Thermodynamics in particular was in that favourable condition, even though, generally speaking, "textbooks failed to fulfil that unitary commitment". Oettingen specified that "the new exposition of the subject matter" was developed in accordance with a dual approach: for every set of relations, a set of complementary ones emerged. From the typographical point of view, this complementarity led to a two-columns exposition, where two sets of variables, functions, and laws were compared to each other, and sometimes the mathematical symmetries were explicitly stressed [Oettingen 1885, p. 1][23].

The whole body of knowledge of thermodynamics could be based on four "main variables" or parameters, and two kinds of energy. In the left column he put temperature and entropy, and the corresponding energy, which was "the actual energy" [*actuelle Energie*] Q, or in other words the exchanged heat. In the right column he put volume and pressure, and the corresponding energy, which was the "potential energy S", namely the mechanical energy which actually appeared under the form of mechanical work. In brief

$$dQ = t \cdot du,$$

where t was "the absolute temperature" and u "the entropy or Adiabate". Temperature was a measure of the amount of "actual energy of molecules".

$$dS = -p \cdot dv,$$

where p was "the pressure" and v "the specific volume". Pressure was the measure of "the dead energy of the body against the outer wall".

If an exchange of "actual energy" led necessarily to a variation of entropy in the physical system, an exchange of "potential energy" led necessarily to a variation in the volume of the system. In brief

$$du = \frac{dQ}{t}, \qquad dv = \frac{dS}{p}.$$

Conversely, a system at "constant Adiabate" could undergo transformations only by a transfer of "potential energy", and a system at "constant volume" only by a transfer of "actual energy" [Oettingen 1885, pp. 2-3].

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[23] Oettingen's essay was divided into three parts: "General relations of thermodynamics for every state of aggregation" [*Allgemeine Beziehungen der Thermodynamik, für alle Aggregatformen*], "Theory of thermal heat capacity based on a new hypothesis" [*Theorie der thermischen Wärmecapacität auf Grund einer neuen Hypothese*], and "Theory of gases" [*Theorie der Gase*].

In general the state of a system could be described by two parameters among the four t, u, p, v, but the two more meaningful representations corresponded to the choices (u, t) and (v, p). After having discussed about the opportunity to label "Adiabate" or "Entropie" the differential form dQ/T, Oettingen insisted on the physical and linguistic symmetry between thermal and mechanical variables and functions. Within the framework of his combinatorial mathematical physics, many "differential quotients" or "coefficients" found room: among them, some enjoyed a relevant physical meaning and deserved a specific label. For instance,

Coefficients of compression: $\left(\dfrac{dp}{dv}\right)_{u/t}$ $\left(\dfrac{dt}{du}\right)_{p/v}$
Coefficients of expansion: $\left(\dfrac{dv}{dt}\right)_{p/u}$ $\left(\dfrac{du}{dp}\right)_{t/v}$
Coefficients of tension: $\left(\dfrac{dp}{dt}\right)_{v/u}$ $\left(\dfrac{dt}{dp}\right)_{v/u}$.

The unusual typographical choice for subscripts corresponded to the constancy of the two variables. More meaningful it appeared the list of "energy coefficients" or "capacities": among them, the ordinary heat capacities could be found. That list was a dual one indeed: if on the left the list of "heat capacities" [Wärmecapacitäten] was displayed, on the right we can see the list of "work capacities" [Arbeitscapacitäten]. The whole list required series of two adjectives for the substantive "capacity".

Thermal heat capacities:	Thermal work capacities:
$\left(\dfrac{dQ}{dt}\right)_{v} = C_v$	$\left(\dfrac{dS}{dt}\right)_{u} = \varPhi_u$
$\left(\dfrac{dQ}{dt}\right)_{p} = C_p$	$\left(\dfrac{dS}{dt}\right)_{p} = \varPhi_p$
Barometric heat capacities:	Barometric work capacities:
$\left(\dfrac{dQ}{dp}\right)_{v} = F_v$	$\left(\dfrac{dS}{dp}\right)_{u} = \varGamma_u$
$\left(\dfrac{dQ}{dp}\right)_{t} = F_t$	$\left(\dfrac{dS}{dp}\right)_{t} = \varGamma_t$
Metric heat capacities:	Entropic work capacities:
$\left(\dfrac{dQ}{dv}\right)_{t} = L_t$	$\left(\dfrac{dS}{du}\right)_{t} = \varLambda_t$
$\left(\dfrac{dQ}{dv}\right)_{p} = L_p$	$\left(\dfrac{dS}{du}\right)_{p} = \varLambda_p$

[Oettingen 1885, pp. 4-8][24].

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[24] A graphic interpretation of heat and work capacities was available both in (u, t) and (v, p) spaces. In particular, the values of C_v and C_p could be found in the horizontal axes u of the plane (u, t), and the values of $\varGamma_u$ and $\varGamma_t$ could be found on the horizontal axes v of the plane (v, p).

At the same time, other algebraic relations and symmetries emerged.

$$F_v = C_v \left(\frac{dt}{dp}\right)_v \qquad \Phi_u = \Gamma_u \left(\frac{dp}{dt}\right)_u$$

$$L_t = F_t \left(\frac{dp}{dv}\right)_t \qquad \Lambda_p = \Phi_p \left(\frac{dt}{du}\right)_p$$

$$C_p = L_p \left(\frac{dv}{dt}\right)_p \qquad \Gamma_t = \Lambda_t \left(\frac{du}{dp}\right)_t$$

$$F_v \cdot L_t \cdot C_p + C_v \cdot F_t \cdot L_p = 0 \qquad \Phi_u \cdot \Gamma_t \cdot \Lambda_p + \Phi_p \cdot \Gamma_u \cdot \Lambda_t = 0$$

[Oettingen 1885, pp. 9-10].

The above relations could find a meaningful simplification in the case of gases, or precisely the so-called ideal gases. In this case, three conditions had to be fulfilled:

1. the specific heats C_v and C_p had to be constant;
2. the internal energy E depended only on temperature; and
3. the equation of state for ideal gas $p \cdot v = Rt$ was assumed.

In this case, a series of simple relations followed:

$$C_v = \Phi_u = \text{const.}, \qquad C_p = \Phi_u - \Phi_p = \text{const.}, \qquad L_t = p, \qquad \Gamma_t = v, \qquad \Lambda_t = -t$$

[Oettingen 1885, pp. 16-7].

Oettingen was aware of the existence of recent abstract approaches to thermodynamics. In particular, he attempted to link his approach to Helmholtz's recent developments, and in this context the concepts of "free and bound energy" played a relevant role. In reality, in accordance with his dual and complementary framework, he relied on a series of four functions, "free, bound, total and lost energies" ("freie, gebundene, totale und verlorene Energie"). A two-fold representation, and an intrinsic symmetry emerged once again. He first introduced the two functions "bound energy $\mathsf{G} = t \cdot u$" and "lost energy $\mathsf{V} = -p \cdot v$", and then defined "free energy" and "total energy" as

$$\mathsf{F} = E - \mathsf{G} = E - t \cdot u \qquad \mathsf{T} = E - \mathsf{V} = E - (-p \cdot v).$$

The differentiation of the functions yielded:

$$\begin{aligned} dE &= d\mathsf{F} + d\mathsf{G} = dQ + dS & dE &= d\mathsf{T} + d\mathsf{V} = dQ + dS \\ d\mathsf{G} &= t \cdot du + u \cdot dt = dQ + u \cdot dt & d\mathsf{V} &= -p \cdot dv - v \cdot dp = dS - v \cdot dp \\ d\mathsf{F} &= dQ + dS - t \cdot du - u \cdot dt = dS - u \cdot dt & d\mathsf{T} &= dQ + dS + p \cdot dv + v \cdot dp \\ & & &= dQ - (-v \cdot dp) \end{aligned}$$

[Oettingen 1885, pp. 21-2].

The two couples of functions or potentials ($\mathsf{F}; \mathsf{G}$) and ($\mathsf{T}; \mathsf{V}$) allowed physicists to split internal energy into two parts, and the split could be performed in two different ways. Moreover, if the traditional split $dE = dQ + dS$ of the *state function* E did not lead to *state functions* or potentials, the two new splits led to two couples of *state functions*. In Oettingen's dual framework, free energy and total energy appeared as the generalisation of mechanical work and exchanged heat, or better a sort of actual work and heat, once some kind of *disturbing terms* were subtracted. In isothermal and isoentropic processes, the mechanical feature of "free energy" emerged, and conversely the thermal feature of "total energy" emerged in isobaric and iso-volumic processes.

When his discussion is translated into an ordered list of mathematical expressions, the symmetries between the couples $(\mathsf{F};\mathsf{G})$ and $(\mathsf{T};\mathsf{V})$ is really astonishing.

$$\begin{array}{ll}
\text{Iso-thermal processes: } dt = 0 & \text{Iso-baric processes: } dp = 0 \\
d\mathsf{F} = dS \quad d\mathsf{G} = dQ & d\mathsf{T} = dQ \quad d\mathsf{V} = dS. \\
\text{Iso-entropic processes: } du = 0 \text{ and } dQ{=}0 & \text{Iso-volumic processes: } dv{=}0 \text{ and } dS{=}0 \\
d\mathsf{G} = u \cdot dt & d\mathsf{V} = -v \cdot dp \\
d\mathsf{F} = dS - u \cdot dt = dS - d\mathsf{G} & d\mathsf{T} = dQ - (-v \cdot dp) = dQ - d\mathsf{V} \\
\rightarrow dS = d\mathsf{F} + d\mathsf{G} & \rightarrow dQ = d\mathsf{T} + d\mathsf{V}
\end{array}$$

[Oettingen 1885, pp. 21-3][25].

He criticised Helmholtz's concepts of "disordered motion" and "measure of disorder" when referred to entropy, because the "complexity of the concept of Adiabate" required that it was associated with "a plurality of conditions". Moreover, from the point of view of physical dimensions, entropy or Adiabate was quite different from the living force of molecules, however disordered it may be. It appeared to Oettingen that perhaps the concept of "bound energy could be put in connection with a disordered motion", but every "overlap between that disorder and the function u had to be excluded". Entropy was a physical entity not so different from volume, and as such it could never become negative. In a body, "the content of heat could not be completely stolen", in the same way that its volume could also not be. In other words, the content of disordered motion could not vanish: in no way could "absolute immobility" be actually realized [Oettingen 1885, pp. 24-5].

In the last pages of the first part of his essay, Oettingen showed that even Gibbs's third potential $\mathsf{N} = E - tu + pv$ could find room in his mathematical framework: it could be expressed alternatively as

$$\mathsf{N} = \mathsf{F} + \mathsf{T} - E \quad \text{or} \quad \mathsf{N} = E - \mathsf{G} - \mathsf{V}.$$

As a further combinatorial synthesis he displayed the derivatives of the five functions $\mathsf{F}, \mathsf{G}, \mathsf{T}, \mathsf{V}, \mathsf{N}$ with reference to the four basic parameters p, v, t, u. Every derivative could be performed under the condition of constancy of one of the other parameters. In other words, those derivatives had the formal structure

$$\left(\frac{dP_k}{dx_j}\right)_{x_l} \qquad k = 1,2,3,4,5; \quad j,l = 1,2,3,4,$$

where P_k represents the five potentials, and x_k, x_l two among the four basic parameters. As a whole, 60 derivatives could be written down $(5 \times 4 \times 3)$, and each of them corresponded to a specific combination of parameters and "capacities". The list could be reversed, and every basic parameter and every "capacity" corresponded to some derivatives of thermodynamic potentials. In brief:

$$\begin{array}{ll}
u = -\left(\dfrac{d\mathsf{F}}{dt}\right)_v = \left(\dfrac{d\mathsf{G}}{dt}\right)_u = -\left(\dfrac{d\mathsf{N}}{dt}\right)_p; & t = \left(\dfrac{d\mathsf{T}}{du}\right)_p = \left(\dfrac{d\mathsf{G}}{du}\right)_t; \\
v = \left(\dfrac{d\mathsf{T}}{dp}\right)_u = -\left(\dfrac{d\mathsf{V}}{dp}\right)_v = \left(\dfrac{d\mathsf{N}}{dp}\right)_t; & p = \left(\dfrac{d\mathsf{F}}{dv}\right)_t = \left(\dfrac{d\mathsf{V}}{dv}\right)_p.
\end{array}$$

A well-defined symmetry shows that the second line can be obtained from the first by means of the exchanges of potentials $\mathsf{F} \leftrightarrow \mathsf{T}$ and $\mathsf{G} \leftrightarrow \mathsf{V}$, and the exchanges of variables $t \leftrightarrow p$ and $u \leftrightarrow v$.

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[25] With regard to the thermodynamic potentials, he acknowledged the contributions of Massieu, Maxwell, and Gibbs.

With regard to capacities, both thermal and mechanical, internal energy had to be added to the list of potentials to be derived. In brief:

$$\begin{array}{llll}
C_v = \left(\dfrac{dE}{dt}\right)_v, & C_p = \left(\dfrac{d\mathsf{T}}{dt}\right)_p; & \mathit{\Gamma}_u = \left(\dfrac{dE}{dp}\right)_u, & \mathit{\Gamma}_t = \left(\dfrac{d\mathsf{F}}{dp}\right)_v \\[2ex]
F_v = \left(\dfrac{dE}{dp}\right)_v, & F_t = \left(\dfrac{d\mathsf{G}}{dp}\right)_t; & \mathit{\Phi}_u = \left(\dfrac{dE}{dt}\right)_u, & \mathit{\Phi}_p = \left(\dfrac{d\mathsf{V}}{dt}\right)_p \\[2ex]
L_t = \left(\dfrac{d\mathsf{G}}{dv}\right)_t, & L_p = \left(\dfrac{d\mathsf{T}}{dv}\right)_p; & \mathit{\Lambda}_p = \left(\dfrac{d\mathsf{V}}{du}\right)_p, & \mathit{\Lambda}_t = \left(\dfrac{d\mathsf{F}}{du}\right)_t.
\end{array}$$

Once again, we see that the above mentioned symmetries operate between the two couples of every line [Oettingen 1885, pp. 23 and 26-9].

In the end Oettingen pointed out the generality of his approach, which was valid "for any state of aggregation". The choice of basic parameters or variables did not affect such a generality: in particular, the variable v could be replaced by a set of geometrical parameters, "just as Helmholtz had done". Nevertheless the theory required "reversible processes", and he did not specify how the wonderful symmetries of the equations might be preserved in the case of irreversible processes. However he thought he had fulfilled his explicit "intention", namely to collect "into a self-contained system all existing knowledge" on thermodynamics [Oettingen 1885, p. 31].

After four years Planck reviewed Oettingen's essay in the *Annalen der Physik*: he described carefully its content, and the author's specific point of view, which he labelled "dualism". He praised both Oettingen's effort to attain "completeness", and "the new systematic framework" for the "variety of formulae dealing with the theory of heat" [Planck M. 1889, p. 838].

4 From "general equations" to chemistry

In 1891, while he was lecturing at Lille university, the French physicist Pierre Duhem began to outline a systematic design of mathematisation and generalisation of thermodynamics. He published a paper in the *Annales scientifiques de l'École Normale Supérieure*, wherein he displayed what he called the "general equations of thermodynamics". He had already published about twenty papers on different subjects: magnetism, chemical equilibrium, electrolytic solution, capillarity, … In 1886 he had also published a book on thermodynamic potentials and their applications. In general, in Duhem's texts, physical remarks and historical reconstructions are tightly linked to each other: this is one of the long-lasting hallmarks of his scientific practice. In that specific instance he made reference to the recent history of thermodynamics. Apart from Clausius, who "had already devoted a paper to a systematic review on the equations of Thermodynamic", four scientists were credited by Duhem with having carried out "the most important researches on that subject": Massieu, Gibbs, Helmholtz, and Oettingen. If Massieu had managed to derive thermodynamics from a "characteristic function and its partial derivatives", Gibbs had shown that Massieu's functions "could play the role of potentials in the determination of the states of equilibrium" in a given system. If Helmholtz had put forward "similar ideas", Oettingen had given "an exposition of thermodynamics of remarkable generality". Duhem did not claim that he would have done "better" than the scientists quoted above, but he thought that there was real "interest" in putting forward "the analytic development of the mechanical Theory of heat", making recourse to "very different methods". He did not mention J.J. Thomson, but his general aim was not so different from Thomson's. However two important differences were at stake: first, he aimed at widening the formal structure of analytical mechanics rather than conflating it with thermodynamics, and second, he rejected any microscopic representation of heat [Duhem 1891, pp. 231-2][26].

In the first section, "Etude thermique d'un système dont on se donne les équations d'équilibre", he took into account a system whose elements had the same temperature: the state of the system could be completely specified by giving its temperature ϑ and n other independent quantities α, β, …, λ. He then introduced some "external forces", which depended on α, β, …, λ and ϑ, and held the system in equilibrium. A virtual work $d\tau_e = A \cdot \delta\alpha + B \cdot \delta\beta + \dots L \cdot \delta\lambda + \Theta \cdot \delta\vartheta$ corresponded to such forces, and a set of $n+1$ equations corresponded to the condition of equilibrium of the physical system:

$$\begin{aligned} A &= f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta) \\ B &= f_\beta(\alpha, \beta, \dots, \lambda, \vartheta) \\ &\dots \\ L &= f_\lambda(\alpha, \beta, \dots, \lambda, \vartheta) \\ \Theta &= f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta) \end{aligned}$$ [Duhem 1891, pp. 233-4].

From the thermodynamic point of view, every infinitesimal transformation involving the generalized *displacements* $\delta\alpha$, $\delta\beta$, …, $\delta\lambda$ and $\delta\vartheta$ had to obey to the first law $dQ = -dU + (1/E)\, d\tau_e$, which could be expressed in terms of the $(n+1)$ generalised Lagrangian coordinates:

$$\begin{aligned} dQ = &- \left(\frac{\partial U}{\partial \alpha} \cdot \delta\alpha + \frac{\partial U}{\partial \beta} \cdot \delta\beta + \dots \frac{\partial U}{\partial \lambda} \cdot \delta\lambda + \frac{\partial U}{\partial \vartheta} \cdot \delta\vartheta \right) \\ &+ \frac{1}{E} \left(A \cdot \delta\alpha + B \cdot \delta\beta + \dots L \cdot \delta\lambda + \Theta \cdot \delta\vartheta \right). \end{aligned}$$

The amount of heat could be written as a sum of $(n+1)$ terms:

$$\begin{aligned} dQ = - \Bigg[&\left(\frac{\partial U}{\partial \alpha} - \frac{A}{E} \right) \cdot \delta\alpha + \left(\frac{\partial U}{\partial \beta} - \frac{B}{E} \right) \cdot \delta\beta + \dots \left(\frac{\partial U}{\partial \lambda} - \frac{L}{E} \right) \cdot \delta\lambda \\ &+ \left(\frac{\partial U}{\partial \vartheta} - \frac{\Theta}{E} \right) \cdot \delta\vartheta \Bigg], \end{aligned}$$

or

$$dQ = - \left[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta \right],$$

wherein

$$R_\alpha = \frac{\partial U}{\partial \alpha} - \frac{A}{E}, \quad R_\beta = \frac{\partial U}{\partial \beta} - \frac{B}{E}, \quad \dots, \quad R_\lambda = \frac{\partial U}{\partial \lambda} - \frac{L}{E}, \quad R_\vartheta = \frac{\partial U}{\partial \vartheta} - \frac{\Theta}{E}.$$

The alliance between mechanics and thermodynamics led to a sort of symmetry between thermal and mechanical quantities. The $n+1$ functions R_α, R_β, …, R_λ, R_ϑ, which Duhem re-wrote as R_α, R_β, …, R_λ, C, played the role of *generalized thermal capacities*, and the last term C was nothing else but the ordinary thermal capacity: in

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[26] Duhem specified that the paper stemmed from his activity as a lecturer "de la Faculté de Sciences de Lille". See *Ibidem*, p. 232. From the Duhem theoretical context it is clear that the expression "mechanical Theory of heat" cannot be interpreted in the same sense as Maxwell and Boltzmann. For a historical reconstruction of Duhem's researches on theoretical physics see the recent Bordoni 2012a and Bordoni 2012b, and the definitely less recent but very detailed Manville O. 1927. For biographical information, see Brouzeng 1981b, pp. 141-15. Jaki 1984 is an accurate biography/hagiography.

some way, the second typographical choice re-established the traditional asymmetry [Duhem 1891, p. 234].

In the context of the generalised theory, the functions internal energy U and entropy S also emerged as two basic state-functions.

> *We start from a physical system in equilibrium under the effect of forces associated with the virtual work*
>
> $$d\tau_e = A \cdot \delta\alpha + B \cdot \delta\beta + \ldots L \cdot \delta\lambda + \Theta \cdot \delta\vartheta.$$
>
> *An infinitesimal modification of the state of equilibrium releases the quantity of heat*
>
> $$dQ = -\left[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \ldots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta\right].$$
>
> *In order to satisfy the two fundamental principles of Thermodynamics, it is necessary and sufficient that the two quantities*
>
> $$\left(R_\alpha + \frac{A}{E}\right) \cdot \delta\alpha + \left(R_\beta + \frac{B}{E}\right) \cdot \delta\beta + \ldots \left(R_\lambda + \frac{L}{E}\right) \cdot \delta\lambda + \left(C + \frac{\Theta}{E}\right) \cdot \delta\vartheta,$$
> $$\frac{R_\alpha}{F(\vartheta)} \cdot \delta\alpha + \frac{R_\beta}{F(\vartheta)} \cdot \delta\beta + \ldots \frac{R_\lambda}{F(\vartheta)} \cdot \delta\lambda + \frac{R_\vartheta}{F(\vartheta)} \cdot \delta\vartheta$$
>
> *are total differentials*[27].

Two series of mathematical relationships

$$\frac{\partial R_\alpha}{\partial\beta} - \frac{\partial R_\beta}{\partial\alpha} = -\frac{1}{E}\left(\frac{\partial A}{\partial\beta} - \frac{\partial B}{\partial\alpha}\right), \ldots, \frac{\partial R_\alpha}{\partial\vartheta} - \frac{\partial C}{\partial\alpha} = -\frac{1}{E}\left(\frac{\partial A}{\partial\vartheta} - \frac{\partial\Theta}{\partial\alpha}\right).$$
$$\frac{\partial}{\partial\beta}\frac{R_\alpha}{F(\vartheta)} = \frac{\partial}{\partial\alpha}\frac{R_\beta}{F(\vartheta)}, \ldots, \frac{1}{F(\vartheta)}\left(\frac{\partial R_\alpha}{\partial\vartheta} - \frac{F'(\vartheta)}{F(\vartheta)}R_\alpha\right) = \frac{1}{F(\vartheta)}\frac{\partial C}{\partial\alpha}$$

led to a series of equations of the kind

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

As Duhem remarked, this equation says that the $n+1$ differential coefficients A, B, …, L, and Θ, "cannot be chosen arbitrarily". In particular it suggested that "a uniform, finite, and continuous function $\mathrm{F}(\alpha, \beta, \ldots, \lambda, \vartheta)$ of $n+1$ coordinates α, β, …, λ, and ϑ there exist". In other words, apart from Θ, which was "independent of the function F", generalised forces could be written as the components of F gradient:

$$A = \frac{\partial}{\partial\alpha}\mathrm{F}(\alpha, \beta, \ldots, \lambda, \vartheta), \quad B = \frac{\partial}{\partial\beta}\mathrm{F}(\alpha, \beta, \ldots, \lambda, \vartheta), \quad \ldots \quad L = \frac{\partial}{\partial\lambda}\mathrm{F}(\alpha, \beta, \ldots, \lambda, \vartheta)$$

[Duhem 1891, pp. 237-8].

According to Duhem, "the mechanical determination of the system" required firstly the specification of the function F, and then the deduction of the generalized forces A, B, …, L, and Θ, and the "thermal coefficients" R_α, R_β, …, and R_λ. His vocabulary swung freely between the mechanical and the thermal poles: the fact is that both the series of generalized forces and generalized thermal coefficients had *mechanical* and *thermal* meaning. He thought that, from the formal point of view, he had really perfected the design he had already outlined in the 1880s: the derivation

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[27] Duhem 1891, p. 236. Duhem acknowledged that his mathematical and physical approach had already been outlined by Clausius, Kirchhoff, and Reech in the 1850s and 1860s. See *Ibidem*, p. 237.

of mechanical and thermal features of a physical system from the potential F and the function Θ [Duhem 1891, p. 251][28].

In 1892 Duhem submitted a long paper with the very general title "Commentaires aux principes de la Thermodynamique" to the *Journal de mathématiques pures et appliquées*. It was the first part of a sort of trilogy whose second and third parts were hosted by the *mathematical* journal in 1893 and 1894 respectively. The set of three papers, when considered as a whole, was nothing less than a treatise on thermodynamics.

He pointed out the difference between the physical quantities which preserved their values over time, and those which did not: mass and electric charge belonged to the first set, while kinematical parameters belonged to the second one. He qualified the former as those which "define the nature of the system", and the latter as those which "define the state": he labelled $A, B, \ldots$, and L the elements of the first set, and α, β, ..., and λ the elements of the second. Matter could be described geometrically by some functions of Lagrangian parameters α, β, ..., λ: among state quantities Duhem distinguished those which appeared explicitly in those equations from those which did not appear. He reserved the labels α, β, ..., and λ for the former, and introduced new labels a, b, ..., l for the latter: in some way he separated geometrical quantities from other quantities. In the latter subset Duhem placed temperature, a quantity which would have played "a remarkable role in the present work". According to Duhem, temperature was not a "quantitative feature" of a physical system: a given value of temperature could be "reproduced, increased and decreased", but temperature did not have the additive property. Temperature could not *measure* literally, but only *locate* the different levels of heat. Moreover, temperature could not be univocally defined: after having defined a temperature ϑ, any continuous and increasing function $\Theta = f(\vartheta)$ could play the role of temperature [Duhem 1892, pp. 276, 278-9, 284 and 286-8][29].

Consistently with the separation between geometrical and "state" coordinates, he introduced two sets of "*thermal coefficients*", R_α, R_β, ..., R_λ, and R_a, R_b, ..., R_l, such that

$$ER_\alpha = \left(E\frac{\partial U}{\partial \alpha} - A\right) - \left(\frac{\partial \mathsf{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathsf{T}}{\partial u}\right), \quad ER_\beta = \ldots, \quad ER_\lambda = \ldots$$

$$E\mathsf{R}_a = \left(E\frac{\partial U}{\partial a} - \mathsf{A}\right), \quad E\mathsf{R}_b = \ldots, \quad E\mathsf{R}_l = \ldots$$

$$dQ = -\left[(R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \ldots R_\lambda \cdot \delta\lambda) + (\mathsf{R}_a \cdot \delta a + \mathsf{R}_b \cdot \delta b + \ldots + \mathsf{R}_l \cdot \delta l)\right].$$

In the first set of equations, geometrical parameters involved the motion of the physical system as a whole, and ordinary Lagrangian terms appeared. On the right-hand side of the last equation, the first round brackets contained the effect of mechanical actions,

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[28] An algebraic mismatch tainted Duhem's derivations, because he made use of two different expressions for entropy: $dQ/F(\vartheta) = dS$ (p. 236) and $\delta S = -dQ/F(\vartheta)$ (*Ibidem*, p. 251).

[29] Paul Needham has recently translated Duhem's *Commentaire* into English [Needham (ed.) 2011]. According to Duhem, temperature stemmed from the concept of "equally warm", and could replace that concept in the definition of equilibrium: "if an isolated system is in equilibrium, the temperature ϑ has the same value everywhere". In the second chapter, he tried to clarify some basic physical concepts: closed cycle, work, kinetic and potential energies, internal energy, the additive property of work, and the principle of the conservation of energy. He stressed the status of "physical hypothesis" of that principle: it was submitted to experience, and it could not be demonstrated, but only put forward by means of some physical considerations [Duhem 1892, pp. 291-307]. Olivier Darrigol showed that Duhem had been inspired by Helmholtz's 1887 discussion on the foundation of measurement in science [Darrigol 2003].

and the second the effects of other kinds of *influences*: the latter was a generalization of the term R_ϑ which Duhem had introduced in 1891. Virtual work was the sum of three components, since actions split into *forces* and *influences*: $d\tau = d\tau_1 + d\tau_2 + d\tau_3$, where

$$d\tau_1 = (A \cdot \delta\alpha + \ldots), \quad d\tau_2 = (\mathsf{A} \cdot \delta a + \ldots), \quad d\tau_3 = \left[\left(\frac{\partial \mathsf{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathsf{T}}{\partial u}\right)\delta\alpha + \ldots\right]$$

[Duhem 1892, pp. 320-1].

Duhem's generalised mechanics/thermodynamics became a sort of analytical thermodynamics, and ordinary mechanics could be looked upon as one of its specific implementations. In order to derive ordinary mechanics from his thermodynamics, he assumed that $dQ = 0$, and all "thermal coefficients" vanished. In this case, the equations became

$$\left(E\frac{\partial U}{\partial \alpha} - A\right) - \left(\frac{\partial \mathsf{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathsf{T}}{\partial u}\right) = 0, \quad \ldots,$$

$$E\frac{\partial U}{\partial a} - \mathsf{A} = 0, \ldots$$

Since the first set of equations corresponded to Lagrange's equations of rational mechanics, the derivation seemed successfully achieved. Nevertheless, a question arose: could the physical derivation be reversed? In other words, are we sure that, when ordinary mechanics is at stake, all thermal coefficients vanish? At that stage, Duhem could not satisfactorily answer the question, and he acknowledged that further theoretical investigations were required. At the end of Duhem's 1892 paper, the nature of the formal relationship between mechanics and thermodynamics was waiting for a complete clarification [Duhem 1892, p. 324].

In 1894, in the third part of his *Commentaire.* he astonished the readers because of the reference to an Aristotelian interpretation of the word "motion": not only was motion looked upon as a kinematic process, but as transformation in general. It is worth quoting Duhem's whole passage.

> In this chapter, not only will we make use of the word *motion* for a change of position in space but also for any change of state, even though it is not accompanied by a displacement. As a consequence we speak of motion when the variables $a, b, \ldots, l$ change whereas the variables $\alpha, \beta, \ldots, \lambda$ keep constant values. In this context, the word *motion* is not in opposition to the word *rest* but rather to the word *equilibrium*[30].

Then he opened another pathway: instead of starting from general equations, he started from the case of thermal equilibrium ($dQ = 0$), which corresponded to the specific mechanical instance, and introduced a perturbation, which represented a source of irreversibility for the physical system:

$$A' - \frac{\partial \mathsf{F}}{\partial \alpha} + \left(\frac{\partial \mathsf{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathsf{T}}{\partial \alpha'}\right) = -f_\alpha, \ldots, L' - \frac{\partial \mathsf{F}}{\partial \lambda} + \left(\frac{\partial \mathsf{T}}{\partial \lambda} - \frac{d}{dt}\frac{\partial \mathsf{T}}{\partial \lambda'}\right) = -f_\lambda.$$

The new functions $f_\alpha, f_\beta, \ldots, f_\lambda$ represented "passive resistances to be overcome by the system". Those resistances depended on basic parameters α, β, …, λ, ϑ, their time derivatives $\alpha', \beta', \ldots, \lambda'$, and time t: from the mathematical point of view, they were "resistances" in the usual mechanical sense. Equilibrium was *perturbed* by actions

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[30] Duhem 1894a, p. 222.

which were the generalisation of mechanical *friction*: the total work $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \ldots + f_\lambda \cdot d\lambda$ could be associated to that kind of actions. Once again, for his generalized thermodynamics, Duhem chose a generalisation of the traditional mechanical lexicon. He was transforming the meaning of mechanical concepts and words, in order to set up a new generalized and Aristotle-flavoured physics [Duhem 1894a, pp. 223-4][31].

Unfortunately the last n equations depended on the $n + 1$ Lagrangian parameters α, β, ..., λ, and ϑ, and Duhem did not have at his disposal a mechanical generalization for the equation corresponding to the parameter ϑ. He was forced to look for the missing equation outside the field of his formal structure: purely thermal processes, involving only temperature changes over time, could not naturally emerge from his theoretical generalisation. Nevertheless, he dared to widen the formal structure of the "thermal coefficients" he had introduced in 1891, and had subsequently generalized in the first Part of his *Commentaire*. The updated version was only slightly different, since it contained the generalized resistances:

$$ER'_\alpha = \left(E\frac{\partial U}{\partial \alpha} - A'\right) - \left(\frac{\partial \mathrm{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathrm{T}}{\partial u}\right) + f_\alpha, \ldots$$

In the ϑ-component of this series of equations, the term representing the passive resistance was missing: it had not been put forward at the beginning, and it could not be found at the end [Duhem 1894a, pp. 224-6].

Consistently with the conceptual framework of a generalized mechanics, he put forward a "fundamental hypothesis" on the passive *resistances* $f_\alpha, f_\beta, \ldots, f_\lambda$: the work done by them could be only null or negative. That hypothesis allowed Duhem to attain a meaningful result concerning the second Principle of thermodynamics. If in 1891

$$dS = \frac{dQ}{F(\vartheta)} = \frac{-[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \ldots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta]}{F(\vartheta)},$$

in 1894

$$\begin{aligned}\frac{dQ}{F(\vartheta)} &= \frac{-[R'_\alpha \cdot \delta\alpha + \ldots R'_\lambda \cdot \delta\lambda + C \cdot \delta\vartheta]}{EF(\vartheta)}\\ &= -dS - \frac{f_\alpha \cdot d\alpha + \ldots + f_\lambda \cdot d\lambda}{EF(\vartheta)}.\end{aligned}$$

For a closed cycle, $\int dS = 0$, and therefore

$$\int \frac{dQ}{F(\vartheta)} = -\int \frac{f_\alpha \cdot d\alpha + \ldots + f_\lambda \cdot d\lambda}{EF(\vartheta)}.$$

If

$$f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \ldots + f_\lambda \cdot d\lambda \leqslant 0, \quad \text{then} \quad \int \frac{dQ}{F(\vartheta)} \geqslant 0.$$

Duhem could finally identify the work $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \ldots + f_\lambda \cdot d\lambda$ with Clausius's "uncompensated work" [Duhem 1894a, pp. 228-9].

Generalised resistances allowed him to re-interpret entropy: in an isolated system, $dQ = 0$, and

$$dS = -\frac{f_\alpha \cdot d\alpha + \ldots + f_\lambda \cdot d\lambda}{EF(\vartheta)}.$$

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[31] In this case the symbolic mismatch seems quite puzzling: in 1891 Duhem had made use of the functions $f_\alpha, f_\beta, \ldots, f_\lambda$ in order to express explicitly the dependence of external forces on the basic parameters, namely $A = f_\alpha(\alpha, \beta, \ldots, \lambda, \vartheta)$ and so on. In 1894, the new *dissipative forces* $f_\alpha, f_\beta, \ldots, f_\lambda$ had to be added to the already existing forces $A', B', \ldots, L'$.

Because of the positive value of the right-hand side of the equation, the left-hand side, namely entropy, was positive as well: no transformation in isolated systems could "make the entropy of the system increase" [Duhem 1894a, p. 229].

The concept of thermal dissipation in natural phenomena was mathematically dressed with the clothes of mechanical dissipation. The second principle of thermodynamics had therefore received a mechanical interpretation, but that interpretation was mechanical in a sense to be carefully specified. As I have already stressed, we are not dealing here with a microscopic mechanical explanation of macroscopic thermodynamic effects. We find a macroscopic mechanical re-interpretation, linked to a re-interpretation of the word "motion" in a new Aristotelian perspective.

At the end of the third Part of his *Commentaire*, Duhem outlined some general "Conclusions", where he put his approach to mechanics and thermodynamics into a historical perspective. He identified two different pathways to thermodynamics. On the one hand, most of the founding fathers of thermodynamics had tried to transform thermodynamics into "an application of Dynamics". They had interpreted heat as "the microscopic and very fast motion of particles which form ordinary bodies", and temperature as the "average living force" corresponding to those motions. On the other hand, other physicists had tried to found thermodynamics "on its own principles". They had not put forward "hypotheses on the nature of heat"; neither had they "borrowed theorems from rational mechanics". The former had managed to successfully interpret the first Principle, namely the Principle of conservation of energy, but had failed to explain the second Principle or "Carnot's Principle". In spite of their "daring efforts", Clausius, Boltzmann and Helmholtz "had not managed to make Carnot's principle stem from the laws of Dynamics in a satisfactory way" [Duhem 1894a, pp. 284-5].

He claimed that he had undertaken a third pathway: thermodynamics as a wide-scope theory of transformations. His design can be looked upon as a reduction of physics to the language of analytical mechanics, but at the same time, as an anti-reductionist design, which involved a deep re-interpretation of that language. In Duhem's "more general science" we find the coexistence of a mechanical approach, in the sense of Lagrange's mathematical physics, and the rejection of "a mechanical explication of the Universe", in the sense of specific mechanical devices.

> In the present work we have attempted to point out a third relationship between Dynamics and Thermodynamics: we have transformed Dynamics into a specific instance of Thermodynamics, or better we have associated the label Thermodynamics with a science which encompasses every kind of transformations, both the change of place and the change of physical qualities, under unifying principles. [...] We can better understand that the change of position in space is not a simpler modification than the change of temperature or some other physical qualities, and we can free ourselves from what has been until now the most dangerous trap of theoretical Physics, namely the search for a mechanical explanation of the universe[32].

In 1896, Duhem published a long essay, *Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques*, which had the dimension of a book The *structural* analogy based on analytical mechanics, was exploited to its extreme consequences, and gave rise to very general equations. At that time he held the chair of theoretical physics at Bordeaux University. He had been appointed to Bordeaux in 1894, and the following year his academic position was transformed into a chair of theoretical physics [Brouzeng 1987, p. 163; Jaki 1984, pp. 122-31].

The *Introduction* to the essay was a theoretical and historical summary intensely focused on the concept of "false equilibrium" that he had introduced three years before

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[32] Duhem 1894a, p. 285.

in his *Introduction à la mécanique chimique*. He briefly analysed the series of thermochemical theories subsequently put forward in the course of the nineteenth century. Duhem reminded the reader that the more ancient theories had identified chemical combinations with exothermal reactions, and chemical decompositions with endothermic ones. Then a "law of displacement of equilibrium" had come forward: "exothermal combinations take place spontaneously at low temperatures" but "decompose spontaneously at high temperatures". Endothermic combinations were expected to behave in the opposite way. Nevertheless the law seemed "in opposition to a huge number of specific instances" [Duhem 1896, pp. 2-4][33].

In other words, there was a wide range of temperature where equilibrium was maintained by a sort of *laziness* of the system: only over and under that region the system became sensitive to temperature. Even in simple systems, for instance mixtures of oxygen, hydrogen and water steam, there were "infinite states of equilibrium, and those states of equilibrium formed a continuous set" [Duhem 1896, p. 5]. For the mathematical and physical interpretation of such phenomena, Duhem could rely on the structural analogy between chemical "false" equilibrium and mechanical "friction". He took into account a very simple configuration: a body sliding on an inclined plane. According to the "theorems of classic mechanics", the body cannot be in equilibrium "under the action of gravity". In reality, for every real plane, "there will be equilibrium when the inclination of the plane is under a certain limiting value". Duhem remarked that, in order to explain "this contradiction", the current explanation was that "the body *rubs* against the plane", and "*classic mechanics does not take into account friction*". The situation could be described in words not so different from those employed to describe chemical false equilibria.

> Whenever classic mechanics, wherein friction is excluded, requires that the physical state of the system is an equilibrium state, our experience confirms such conclusion. Nevertheless, the system might be in equilibrium even in states which are not equilibrium states from the point of view of frictionless mechanics[34].

The general equations he had put forward in 1894 contained the forces $A, B, \ldots, L$, the gradient of the potential F, viscous forces, and the Lagrangian terms involving the kinetic energy of the system as a whole T. In accordance with a more synthetic typographic representation,

$$\begin{aligned}
&A, B, \ldots, L \rightarrow \mathsf{A}, \mathsf{B}, \ldots, \mathsf{L} \\
&\frac{\partial \mathsf{F}}{\partial \alpha}, \frac{\partial \mathsf{F}}{\partial \beta}, \ldots, \frac{\partial \mathsf{F}}{\partial \lambda} \rightarrow \varPhi_a, \varPhi_b, \ldots, \varPhi_l \\
&f_\alpha, f_\beta, \ldots, f_\lambda \rightarrow \varphi_\alpha, \varphi_\beta, \ldots, \varphi_\lambda \\
&\frac{\partial \mathrm{T}}{\partial \alpha} - \frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \alpha'}, \frac{\partial \mathrm{T}}{\partial \beta} - \frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \beta'}, \ldots, \frac{\partial \mathrm{T}}{\partial \lambda} - \frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \lambda'} \rightarrow J_a, J_b, \ldots, J_l,
\end{aligned}$$

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[33] As in his 1893 book on "mechanical chemistry", Duhem discussed the case of oxygen, hydrogen and water, when "gaseous water is produced at the expense of oxygen and hydrogen, and accompanied by a great release of heat". Scientists expected that, at low temperatures, "most of the gas under consideration would be in the state of steam", and when the temperature increased, "the amount of steam in the system decreases". Nevertheless, the expected behaviour had been really observed only at a high temperature. On the contrary, at low temperatures, under a given threshold, "a mixture of oxygen, hydrogen and steam" was observed in equilibrium, "irrespective of its composition". Only under the threshold, at a temperature "close to sombre red", the mixture underwent combination. Similar "contradictions" were even offered by "endothermic combinations": at high temperatures, silver oxide was produced as expected, but, "at temperatures less than 100 °C, silver oxide did not decompose", differently from what scientists had expected.

[34] Duhem 1896, p. 8.

the equations of motion were formally expressed by the equations

$$\begin{aligned}
&\mathsf{A} - \Phi_a + J_a + \varphi_a = 0\\
&\mathsf{B} - \Phi_b + J_b + \varphi_b = 0\\
&\ldots\\
&\mathsf{L} - \Phi_l + J_l + \varphi_l = 0 \quad \text{[Duhem 1896, pp. 67-8 and 70-2].}
\end{aligned}$$

From the structural point of view, every equation was of the sum of four terms: generalised forces or actions, derivatives of the thermodynamic potential, "inertial" terms, and "viscous" terms. At this point Duhem introduced a "*fundamental hypothesis*", which was nothing else but a new term in the equations of motion:

$$\begin{aligned}
&\mathsf{A} - \Phi_a + J_a + \varphi_a + g_a\frac{a'}{|a'|} = 0\\
&\mathsf{B} - \Phi_b + J_b + \varphi_b + g_b\frac{b'}{|b'|} = 0\\
&\ldots\\
&\mathsf{L} - \Phi_l + J_l + \varphi_l + g_l\frac{l'}{|l'|} = 0.
\end{aligned}$$

The new functions g_a, $g_b, \ldots$, g_l were negative functions, and depended on the Lagrangian parameters a, $b, \ldots$, l, their time-derivatives a', $b', \ldots$, l', and the forces $\mathsf{A}, \mathsf{B}, \ldots, \mathsf{L}$. Differently from the "viscous" forces φ_α, $\varphi_\beta, \ldots$, φ_λ, they did not vanish when the velocities vanished: on the contrary, they tended to the limiting functions γ_α, $\gamma_\beta, \ldots$, γ_λ, which depended only on a, $b, \ldots$, l and $\mathsf{A}, \mathsf{B}, \ldots, \mathsf{L}$. The terms of the kind $g_a \cdot a'/|a'|$ represented the generalisation of static friction which had been discussed in the *Introduction*: this explains why they could not vanish together with the generalised velocities. As expected, the "*work done by friction*",

$$\left(g_a\frac{a'^2}{|a'|} + g_b\frac{b'^2}{|b'|} + \ldots + g_l\frac{l'^2}{|l'|}\right) dt,$$

was negative [Duhem 1896, pp. 72-5][35].

Two different conditions of equilibrium emerged. The first corresponded to parameters and the external actions which suffered friction; the second corresponded to the six parameters which described the purely mechanical motion "of the system as a whole". The latter was nothing else but the condition of equilibrium for an "invariable solid body".

$$\begin{cases}\gamma_a \leqslant \mathsf{A} - \Phi_a \leqslant -\gamma_a\\ \gamma_b \leqslant \mathsf{B} - \Phi_b \leqslant -\gamma_b\\ \ldots\\ \gamma_l \leqslant \mathsf{L} - \Phi_l \leqslant -\gamma_l\end{cases} \quad \text{and} \quad \begin{cases}\mathsf{M} - \Phi_m = 0\\ \ldots\\ \mathsf{N} - \Phi_n = 0.\end{cases}$$

The first set of inequalities described the "*infinite states of equilibrium, which classic thermodynamics was not able to foresee*": they exhibited that structural analogy with static friction which Duhem had already put forward in the *Introduction*.

The following steps offered no surprise, and he took care of specifying that his words and concepts were in tune with Clausius's original approach. The "total

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[35] Mathematical terms of this kind had already been put forward by Duhem in his papers of hysteresis (Duhem 1894b, Duhem 1895a, and Duhem 1895b).

transformation" dQ/T was the sum of the "compensated" term $-dS$ and the "uncompensated" term corresponding to "viscosity" and "friction":

$$\frac{dQ}{T}+dS=-\frac{1}{ET}\left(\varphi_a a'+\varphi_b b'+\ldots+\varphi_l l'\right)dt-\frac{1}{ET}\left(g_a\frac{a'^2}{|a'|}+g_b\frac{b'^2}{|b'|}+\ldots+g_l\frac{l'^2}{|l'|}\right)dt$$

[Duhem 1896, pp. 77 and 83-4][36].

Duhem had found a general and pliable mathematical structure, which could fit the specific features of specific systems, and could be further widened in order to account for phenomena of increasing complexity.

In the second Part of his book, Duhem continued to bridge the gulf between physics and chemistry, and in particular tried to catch mathematically the specific processes taking place in chemistry. For this purpose, he assumed that the equations corresponding to the Lagrangian coordnates $\alpha, \beta, \ldots, \lambda$ did not contain "inertial" terms:

$$\begin{aligned}&\mathsf{A}-\Phi_a+\varphi_a+g_a\frac{a'}{|a'|}=0\\&\mathsf{B}-\Phi_b+\varphi_b+g_b\frac{b'}{|b'|}=0\\&\ldots\\&\mathsf{L}-\Phi_l+\varphi_l+g_l\frac{l'}{|l'|}=0.\end{aligned}$$

He specified that "variations of living force" and "inertial forces" were excluded. It is worth stressing that Duhem aimed at setting up a general mechanics, which could widen the scope of traditional mechanics. The assumptions he put forward in this part led to a new mechanics, which was a sort of complementary mechanics of the traditional one [Duhem 1896, pp. 89-91].

He called into play the thermodynamic potential $H = \mathsf{F} + PV$, which was a suitable potential for physical-chemical processes taking place at constant pressure, and after a further typographic simplification

$$\begin{aligned}\eta_a&=-\mathsf{A}+\Phi_a\\&\ldots\\\eta_l&=-\mathsf{L}+\Phi_l,\end{aligned}$$

the generalised equations of motion assumed the formal structure

$$\begin{aligned}&\eta_a-\varphi_a-g_a\frac{a'}{|a'|}=0\\&\ldots\\&\eta_l-\varphi_l-g_l\frac{l'}{|l'|}=0\ \text{[Duhem 1896, pp. 92-3]}^{37}.\end{aligned}$$

These equations contained three kinds of terms: if the first corresponded to the derivatives of a thermodynamic potential, the other two corresponded to two kinds of dissipation. It is worth remarking that Duhem had added dissipative terms to Lagrange's

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[36] Duhem 1896, pp. 83-4. A misleading misprint appears in the last equation in Duhem's original text.

[37] Duhem's potential H corresponded to Massieu's potential H' and Gibb's potential ζ.

equations in order to generalise analytical mechanics. When he applied the new mathematical structure to chemical phenomena, no inertial terms appeared, while dissipative terms were in prominence. In a certain way, analytical mechanics and Chemistry represented two opposite poles in the new formal framework.

In the context of Chemistry, he confined himself to systems described by only one Lagrangian parameter α, apart from "a uniform and constant pressure P" and "a variable temperature T", and wrote the *equation of motion* for this simple configuration:

$$\frac{\partial H\left(P,\alpha,T\right)}{\partial\alpha}-\varphi\left(P,\alpha,T,\alpha'\right)-g\left(P,\alpha,T,\alpha'\right)\frac{\alpha'}{|\alpha'|}=0.$$

When dissipative effects vanished, the equation became simply

$$\frac{\partial H(P,\alpha,T)}{\partial\alpha}=0.$$

It represented a curve in the plane (T,α), which corresponded to "the curve of true equilibrium" under constant pressure P. In general, friction did exist, and the condition of equilibrium for the system under consideration was a "specific instance" of the inequalities

$$\gamma(P,\alpha,T)\leqslant\frac{\partial H(P,\alpha,T)}{\partial\alpha}\leqslant-\gamma(P,\alpha,T).$$

The boundaries of the "region of false equilibrium" in the plane (T,α) corresponded to the equations

$$\frac{\partial H(P,\alpha,T)}{\partial\alpha}+\gamma(P,\alpha,T)=0\quad\text{and}\quad\frac{\partial H(P,\alpha,T)}{\partial\alpha}-\gamma(P,\alpha,T)=0$$

[Duhem 1896, pp. 99-101].

The exact shape of the region of false equilibrium could not be specified by the theory, but by experiments: they had shown that the width of the region decreased when temperature increased. The region of false equilibrium was quite wide at low temperatures, while at high temperatures it became a thin strip around the curve of true equilibrium. As Duhem had already pointed out in his 1893 *Introduction à la mécanique chimique*, it was at low temperatures that "states of equilibrium extremely different from those expected on the basis of classic thermodynamics" really occurred. Classic thermodynamics did not take into account the generalisation of the concept of "friction": therefore it could only describe real phenomena at high temperatures. For this reason, as Duhem remarked, "*chemical mechanics gives place to simpler laws at high rather than low temperatures*". The increase of temperature played in chemistry the same role of the increase of smoothness in mechanics. High temperatures dissolved *chemical* friction in the same way that better smoothness dissolved mechanical friction. Duhem remarked that modern mechanics was born when Galileo decided to disregard mechanical friction. He had given birth to a very simplified physics: Duhem was undertaking the demanding task of restoring a complex science for the real world [Duhem 1896, p. 105].

When Duhem focused his attention in particular on the concept of generalised "velocity", the formal analogy between mechanics and Chemistry underwent a critical stress. From the equation

$$\frac{\partial H\left(P,\alpha,T\right)}{\partial\alpha}-\varphi\left(P,\alpha,T,\alpha'\right)-g\left(P,\alpha,T,\alpha'\right)\frac{\alpha'}{|\alpha'|}=0.$$

He tried to derive "the velocity of transformation of the system", or in other words, the velocity of the chemical reaction. The derivation seemed too complex, and he dared to put forward some simplifications involving the two *dissipative* functions $\varphi(P,\alpha,T,\alpha')$ and $g(P,\alpha,T,\alpha')$. He assumed that $g\,(P,\alpha,T,\alpha')$ did not depend on α', and in particular that

$$g(P,\alpha,T,\alpha') \approx \gamma(P,\alpha,T),$$

where the limiting function $\gamma(P,\alpha,T)$ could not depend on α'. Then he assumed that the function $\varphi(P,\alpha,T,\alpha')$, which expressed the "viscosity" of the system, depended on α' in a linear way:

$$\varphi(P,\alpha,T,\alpha') \approx \Phi(P,\alpha,T)\cdot\alpha'.$$

According to these simplifications, the *equations of motion* became

$$\frac{\partial H(P,\alpha,T)}{\partial\alpha} - \gamma(P,\alpha,T) - \Phi(P,\alpha,T)\cdot\alpha' = 0,$$
$$\frac{\partial H(P,\alpha,T)}{\partial\alpha} + \gamma(P,\alpha,T) - \Phi(P,\alpha,T)\cdot\alpha' = 0 \quad \text{[Duhem 1896, p. 128].}$$

The simplified equations allowed Duhem to give a simple expression for the "velocity" of reaction in chemical processes, because α' appeared only in the factorisation of the third term:

$$\alpha' = \frac{\frac{\partial H(P,\alpha,T)}{\partial\alpha} - \gamma(P,\alpha,T)}{\Phi(P,\alpha,T)},$$
$$\alpha' = \frac{\frac{\partial H(P,\alpha,T)}{\partial\alpha} + \gamma(P,\alpha,T)}{\Phi(P,\alpha,T)}.$$

The generalised "velocity" could increase because of two different effects: the increase of the numerator or the decrease of the denominator. The numerator increased when the system drifted away from the two borderlines of the region of false equilibrium, wherein

$$\frac{\partial H(P,\alpha,T)}{\partial\alpha} = +\gamma(P,\alpha,T) \quad \text{or} \quad \frac{\partial H(P,\alpha,T)}{\partial\alpha} = -\gamma(P,\alpha,T).$$

The denominator decreased when "viscosity" decreased, namely when the system approached classic thermodynamic behaviour [Duhem 1896, pp. 129 and 131][38].

When the generalised viscosity vanished, velocity became infinite. The general equations Duhem had put forward in the second part of his 1896 book contained both inertial and dissipative terms. When he let dissipative terms drop, a re-interpretation of modern mechanics re-emerged. When he let inertial terms drop, some mathematical simplifications led him to a new mechanics for chemical processes. Pure mechanics and chemical reactions represented the opposite poles in Duhem's *Energetics*, and the existence of such poles could be looked upon as the result of a powerful unification. The unifying power of Duhem's equations could encompass physics and chemistry in a common mathematical framework: physics and chemistry appeared as different implementations of a very general formal structure[39].

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[38] There are some plus/minus misprints in Duhem's equations.

[39] Duhem stressed that the new *chemical mechanics* could be looked upon as a re-interpretation of Aristotle's natural philosophy: his pliable mathematical structure could host both modern and ancient science. As Monica Ugaglia pointed out some years ago, the Aristotelian theory of motion dealt originally with processes taking place through some kind of medium: it was not a "kinematic" theory in the modern sense, but rather a "hydrostatic" one, where dissipation was an intrinsic component. In the Aristotelian tradition after Johannes Philoponus, a "hybrid kinematic-hydrostatic system" emerged. According to Ugaglia, in the sixteenth and seventeenth century, Tartaglia, Benedetti and Galileo had to re-discover Aristotle's hydrostatic beneath that hybrid kinematics, in order to overcome it. See Ugaglia 2004, pp. 8-13.

5 A problematic legacy

In general, the contemporaries were not really interested in the subject matter because it lay outside the most exciting fields of research which scientists were undertaking in the last decade of the nineteenth century. Duhem was not discouraged by such lack of interest in the community of theoretical physicists. Neither mathematical nor conceptual difficulties prevented him from inquiring into chemical reactions with the help of his generalised theory: he thought that a rough model for explosive chemical reactions could be deduced from his equations. However Duhem's generalised mechanics attracted some physicists, chemists, and mathematicians around the turn of the twentieth century[40].

In 1898, the mathematical physicist Helm paid great attention to Duhem's theoretical physics. He had become Professor of analytical geometry and mechanics at Dresden University of Technology in 1888, and he had played an important role in the debate on *Energetism* in German speaking countries. Helm opened his book on the history of *Energetics* with a very poetical passage which sealed the paper that Duhem had devoted to the history of Optics in 1894. Helm qualified Duhem as "the ardent proponent of energetics in France", where Energetics was not intended as a specific theory but as "a *unified* development of thought" or "a comprehensive knowledge of nature" ("eine eigenartige Weise umfassender Naturerkenntnis"). It corresponded to a representation of natural processes "as *immediately as possible, without* the aid of invented mechanical devices". It aimed at "a great reorientation in the human understanding of natural events" [Helm 1898, pp. 55 and 65][41].

In the seventh part of the book, Helm mentioned Duhem's mathematical generalisation of "differential work" and "differential heat", which went far beyond the representation of energy as a sum of products between "*intensities*" and "*capacities*" or "*quantity functions*". Helm's general attitude towards mechanics was not so different from Duhem's: he aimed to "make mechanics useful for non-mechanical processes, but without a mechanical hypothesis". For the implementation of that meta-theoretical design he could rely on the principle of conservation of energy ("das Perpetuum-mobile-Prinzip"), and on a "principle of analogy". The latter was nothing else but the structural analogy between the equations of analytical mechanics and the equations describing non-mechanical processes, which Helm attributed to Helmholtz and J.J. Thomson [Helm 1898, pp. 314, 363, and 375-6].

In this context, it is worth stressing the difference between Helm's and Ostwald's Energetics, which I have already outlined in the Introduction. Even more remarkable it is the conceptual gap between the line of research leading from Rankine to Duhem's energetics and Ostwald's kind of energetics. Whereas Duhem developed a sophisticated mathematical theory of thermodynamics and devised a wide mathematical framework for physics and chemistry following the model of Lagrange's mechanics, Ostwald developed a broad physical world-view wherein the concept of matter, which

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[40] Duhem did not manage to encompass all physical and chemical phenomena in his Energetics: electromagnetic phenomena, radioactivity, and radiant heat remained unrepresented. As Deltete and Brenner reminded us, the new interpretations of those phenomena, which emerged at the turn of the twentieth century, involved "microscopic discreteness and discontinuity of the kind forbidden by his energetics" [Brenner and Deltete 2004, p. 223]. See also Brouzeng 1981a, pp. 241-61.

[41] Robert Deltete translated and commented Helm's book, and analysed the debate on energetism [Deltete 1999, and Deltete 2000] At the end of the mentioned paper, Duhem had synthesised his historiographical view, where the superposition of two historical processes was at stake: the short-term turnover of specific physical hypotheses and models, and the long-term progress of physics. The last passage was extraordinary lyrical: this style was unusual for him [Duhem 1894c, p. 125].

he found “indefinite and contradictory,” had to be replaced by the concept of energy [Ostwald W. 1896, pp. 159-60][42].

In 1897 Duhem had published the first volume of the treatise *Traité élémentaire de mécanique chimique, fondée sur la thermodynamique*, and the volume attracted some attention from chemists. In that series of books Duhem developed the theory he had put forward in 1896. The chemist Wilder D. Bancroft wrote a brief review in the American journal *Science*, and the review was really enthusiastic. He had been educated at Harvard, and had worked in Ostwald’s and van ’t Hoff’s laboratories; the year before he had founded the *Journal of Physical Chemistry*. He stressed that the book was “doubly valuable”, because it offered “the mathematical development of the subject”, and that development was presented “in a masterly way”. Bancroft acknowledged that at that time “the mathematical treatment of physical chemistry in books” was “painfully deficient” when compared to “the exhaustive handling of the experimental side of the subject” which had been offered by Ostwald. He found that the second part of the book, which was devoted to “false equilibria and explosions” was “more interesting than the first part” because the point of view was “less familiar”. Bancroft remarked that the notions of “viscosity” and false equilibria could be better understood “by an analogy from mechanics”. In particular, the application of Duhem’s mathematical theory “to the point of reaction, to reaction velocities and to explosions” deserved “careful attention” [Bancroft 1897, pp. 625-6][43].

The following year Bancroft reviewed the second volume of Duhem’s book, and his enthusiasm did not soften: he found that the book attempted “to present exact theory in such a form as to be applicable to experimental data and not to hypothetical or simplified phenomena”. Although that goal was difficult to attain, Duhem’s volume came “nearer to it than anything that has yet been published” [Bancroft 1898, p. 215].

Bancroft’s third review was quite different: in the meantime his enthusiasm had transformed into disappointment. He acknowledged that he had in front of him “an exhaustive study of chemical equilibrium put into mathematical form”, but that application of mathematics to chemistry was “unfortunately more ornamental than useful”. Differently from what he had stated the year before, he lamented that only a few of “the myriads of formulas” could be applied “to any concrete case”. The key point was the relationship between theory and experimental practice: Duhem’s volumes offered a new language and a new framework for chemistry, but chemists were not at ease with that mathematical and theoretical approach. Some of them were fascinated at a first reading, but in the end they were dissatisfied, because the gap between theory and the actual laboratory practice could not be easily bridged. From the point of view of a historical reconstruction, we have to take note of the dissatisfaction of a laboratory chemist with a mathematical approach which he did not master [Bancroft 1899, p. 82].

In 1905 the *American Association for the Advancement of Science* charged the physicist Carl Barus with giving “an account of the advances made in physics during the nineteenth century”. He was one of the American scientists who had studied in Europe and had received their Ph.D. from a German University: he had spent four

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[42] According to Anastasios Brenner, Ostwald’s energetism represented a sort of “disproportional” answer to atomism [Brenner 1990, pp. 82 and 86]. It is worth mentioning that, in the 1960s, the physical chemist Donald G. Miller wrote that Duhem “belonged to the community of energetists, together with Ernst Mach, Georg Helm, and Wilhelm Ostwald” [Miller 1967, p. 447]. The warm relationship between Duhem and Ostwald cannot be interpreted as an agreement on the meaning and practice of Energetics. On their friendship, see Brouzeng 1981b, pp. 226-8. For a clear and synthetic analysis of the differences between Duhem’s Energetics and Ostwald’s and Helm’s Energetics, see Needham 2011, p. vii.

[43] On the role of Bancroft in the history of physical chemistry, see Servos 1990, chapter 4, and Laidler 1993, pp. 48-50, 125, and 292-3.

years at Würzburg with Kohlrausch. Barus stressed "the analytical power" of thermodynamic potentials, and mentioned the contributions of Gibbs, Massieu, Helmholtz, Planck, and Duhem. He pointed out "the introduction of a virtual thermodynamic modification in complete analogy with" analytical mechanics, Gibbs's contribution to "the brilliant advance of chemical statics", and "the progress of chemical dynamics", which had been favoured by Helmholtz, and "with much skill" by Duhem and the Polish physicist Wladislaw Natanson [Barus 1905, pp. 353 and 364; Lindsay 1937, p. 484].

The competition between a more formal and more mathematical approach to chemical processes, on the one hand, and a more pragmatic approach, on the other, crossed the history of chemistry in the last decades of the nineteenth century. In this context, it is worth mentioning the debate between the theoretical chemist Johannes van Laar and Walther Nernst, which started in 1896 and went on for some years. Van Laar put forward a sophisticated mathematical approach to chemistry, which culminated in the treatise he published in 1901, *Lehrbuch der mathematischen Chemie*, where he stressed the necessity of developing a "mathematical chemistry" besides an "experimental chemistry", on the track of the historical development of physics. He would have endowed chemistry with a suitable mathematical structure "in the same way as Maxwell had dressed Faraday's representation of lines of force" [Kragh and Weininger 1996, pp. 106-7; Laar 1901, pp. VII-VIII].

In the first decades of the twentieth century, some kind of unification between physics and chemistry through a generalisation and re-interpretation of analytical mechanics really took place. The physicist and historian of physics René Dugas pointed out the formal link between Quantum physics and the tradition of analytical mechanics. What we usually call Quantum physics aimed to describe atomic structure and chemical bonds through a re-interpretation of Lagrangian and Hamiltonian formalism, at least in extremely simple configurations. Dugas found a meaningful structural analogy between late nineteenth-century widening of the Lagrangian approach, and the quantum re-interpretation of Hamilton's formalism. He saw them as very different implementations of a similar scientific design [Dugas 1937, p. 70].

In the second half of the nineteenth century some scholars had attempted to bridge the gulf between two traditions that had emerged in the first half: "the *Fourier line*, which considered *workless dissipation*", and "*Carnot line*, which considered *dissipationless work*". After a century the mathematical physicist Clifford A. Truesdell remarked that, in the last decades of the nineteenth century, thermodynamics was sometimes looked upon as "a dead field, insusceptible of broadening or deepening". The majority of physicists had confined themselves to equilibrium states: as a consequence, thermodynamics was "inapplicable to *natural processes*", namely real, irreversible phenomena. Nevertheless the interest in the complexity of the physical world, and in a more sophisticated mathematical approaches to thermodynamics, had never disappeared, and continuously re-emerged in the course of the twentieth century. What Truesdell called "modern continuum thermodynamics" consisted of a "collection" of theories concerning "elastic materials", "viscous materials", "materials with memory", "mixtures", and so on. All these branches of physics were based on the same principle: the "Clausius-Duhem inequality". In brief, "*for any process suffered by any body composed of the material under study*", Rational thermodynamics assumed

$$S - S_0 \geqslant \int \frac{dq}{\vartheta}\bigg|_{process},$$

"*dq denoting the element of heat received from external sources and ϑ the temperature of the part of the system receiving it*". Truesdell claimed that this inequality could be applied to "general motions", far beyond the states of equilibrium: to deny this was to deny "that there can be such a thing as a thermodynamics of irreversible processes" [Truesdell 1984, pp. 7, 24-5, 123 and 157][44].

Conclusion

Different routes towards an abstract thermodynamics were taken by physicists who had different attitudes towards mechanics. In the last decades of the nineteenth century, two kinds of mechanics were available: mechanics as mechanical models like colliding elastic molecules or aethereal vortices on the one hand, and mechanics as a formal language for physical sciences on the other hand. If something like "the crisis of mechanics" crossed the late nineteenth century, it did not dwell at the homes of Massieu, Gibbs, Helmholtz, Planck, Oettingen, and Duhem. These physicists offered *mechanical* theories of heat that relied on fruitful connections between the mathematical language of mechanics and the specific contents of thermodynamics.

They developed structural analogies between thermodynamics and analytical mechanics in different ways: both the adepts and the enemies of the microscopic machinery of matter and aether were involved. Whereas Duhem refused microscopic interpretations of heat, J.J. Thomson incorporated those interpretations in his theoretical approach, and Helmholtz also made recourse to a Lagrangian approach involving fast hidden motions. Different levels of integration between thermal and mechanical effects were also at stake. Whereas Helmholtz and Planck relied on a mere complementarity between mechanical and thermal variables in the expressions of state functions, Oettingen and Duhem explored the possibility of a more demanding symmetry between mechanical and thermal *capacities*[45].

With regard to the interrelations and mutual acknowledgments between the various proponents of abstract thermodynamics, different attitudes emerged. Oettingen explicitly mentioned the role played by Massieu, Gibbs and Helmholtz. In his *Vorlesungen über Thermodynamik* Planck did not name other contributors to the more abstract approach to thermodynamics, except Helmholtz. In the introduction to the first edition (1897), he associated Joule, Waterston, Krönig, Clausius, Maxwell, and Boltzmann with "the kinetic theory", and Helmholtz with a different "thermodynamic method", where "the mechanical theory of heat" rested on the intrinsic link between heat and motion but gave up any "specific representation of the nature of that motion". In the second, improved edition he only added the names of physicists who had contributed to the "research results in the field of heat radiation" [Planck 1897, pp. IV-V; Planck 1905, pp. VI-VII].

Duhem wanted to know the roots of the abstract tradition, and contributed to its history: in his own thermodynamic memoirs, he mentioned and discussed the researches of Massieu, Gibbs, Helmholtz, and Oettingen. He did not mention Planck and J.J. Thomson. He propounded the most original and systematic reinterpretation of thermodynamics, as well as the boldest upgrading of analytical mechanics. From the 1880s onwards, he pursued a wide-scope alliance between Lagrangian mechanics and thermodynamics. That scientific enterprise was not confined to thermodynamics: in the same years, in Great Britain, FitzGerald, J.J. Thomson and Joseph Larmor

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[44] The Clausius-Duhem inequality was explicitly mentioned by Truesdell for the first time in 1960, in the long essay "The Classical Field Theories" he published in 1960 together with Richard Toupin (I thank Sandro Caparrini for this information). In the second half of the twentieth century, other mathematical physicists developed what we call rational thermodynamics: among them, Bernard Coleman and Walter Noll.

[45] Clausius had previously 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.

were looking for a new alliance between Lagrangian mechanics and the electromagnetic theory. Another kind of alliance between abstract mechanics and a field theory cleared of the concept of force led Hertz to a bold geometrization of physics in 1894[46].

To some extent, today's physicists may regard the nineteenth-century quest for an abstract thermodynamics as a body of knowledge of merely historical interest. In reality, this theoretical stream resurfaced in the second half of the twentieth century, and found new implementations in the context of rational thermodynamics and thermodynamics of irreversible processes.

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References

Bancroft W.D. 1897. *Traité élémentaire de mécanique chimique, fondée sur la thermodynamique*. P. Duhem. Vol. I. *Science* **120**: 625-626

Bancroft W.D. 1898. *Traité élémentaire de mécanique chimique, fondée sur la thermodynamique*. By P. Duhem. Vol. II. *Science* **163**: 214-215

Bancroft W.D. 1899. *Traité élémentaire de mécanique chimique, fondée sur la thermodynamique*. By P. Duhem. Vol. III. Vol. IV. *Science* **238**: 81-82

Barus C. 1905. The Progress of physics in the Nineteenth Century. *Science* **22**: 353-369

Bierhalter G. 1993. Helmholtz's Mechanical Foundation of thermodynamics. in Cahan D. (ed.) 1993a, pp. 291-333

Boltzmann L. 1872. Weiteren Studien über das Wärmegleichgewicht unter Gasmolekülen. in Boltzmann L. 1909, I. Band, pp. 317-402

Boltzmann L. 1877. Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht. in Boltzmann L. 1909, II. Band, pp. 164-223

Boltzmann L. 1909. *Wissenschaftlichen Abhandlungen*, Barth, Leipzig

Bordoni S. 2012a. Unearthing a Buried Memory: Duhem's Third Way to thermodynamics. Part 1. *Centaurus* **54**: 124-147

Bordoni S. 2012b. Unearthing a Buried Memory: Duhem's Third Way to thermodynamics. Part 2. *Centaurus* **54**: 232-249

Born M. 1948. Max Karl Ernst Ludwig Planck. 1858-1947. *Obituary Notices of Fellows of the Royal Society* **6**: 161-188

Brenner A. 1990. *Duhem. Science, réalité et apparence*, Vrin, Paris

Brenner A. and R.J. Deltete. 2004. Essay Review on Duhem P. 2002, *Foundations of Chemistry* **6**: 203-232

Bridgman P.W. 1961 (1941). *The Nature of thermodynamics*, Harper & Brothers, New York

Brouzeng P. 1981a. *L'oeuvre scientifique de Pierre Duhem et sa contribution au développement de la thermodynamique des phénomènes irreéversibles*, vol. 1, These (pour obtenir le grade de Docteur d'Etat ès Sciences), Université de Bordeaux I

Brouzeng P. 1981b. *L'oeuvre scientifique de Pierre Duhem et sa contribution au développement de la thermodynamique des phénomènes irreéversibles*, vol. 2 (documents annexes), These (pour obtenir le grade de Docteur d'Etat ès Sciences), Université de Bordeaux I

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[46] According to Hertz, fundamental laws and concepts of mechanics had to be clarified, in order to rebuild a reliable theoretical framework, where "the ideas of force and the other fundamental ideas of mechanics appear stripped of the last remnant of obscurity". This new physics appeared in accordance with the theoretical model of contiguous action. See Hertz H. 1894, "Author's Preface", p. 1, and p. 41.

Brouzeng P. 1987. *Duhem 1861-1916 – Science et Providence*, Belin, Paris

Brown L., M. Riordan and M. Dresden (eds.), pp. 645-684

Buchwald J.Z. 1993. Electrodynamics in context: Object states, laboratory practice, and anti- romanticism. in Cahan D. (ed.) 1993a, pp. 334-373

Cahan D. (ed.) 1993a. *Hermann von Helmholtz and the Foundations of Nineteenth-Century*, University of California Press, Berkeley, Los Angeles, London

Cahan D. 1993b. Introduction: Helmholtz at the Borders of Science. in Cahan D. (ed.) 1993a, pp. 1-13

Clausius R. 1854. Ueber eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie. in Clausius R. 1864, pp. 127-154

Clausius R. 1862. Ueber die Anwendung des Satzes von der Aequivalenz der Verwandlungen auf die innere Arbeit. in Clausius R. 1864, pp. 242-279

Clausius R. 1864. *Abhandlungen über die mechanische Wärmelehre*, erste Abtheilung, Friedrich Vieweg und Sohn, Braunschweig

Clausius R. 1865. Ueber verschiedene für die Anwendung bequem Formen der Hauptgleichungen der mechanischen Wärmetheorie. in Clausius R. 1867, pp. 1-44

Clausius R. 1867. *Abhandlungen über die mechanische Wärmelehre*, zweite Abtheilung, Friedrich Vieweg und Sohn, Braunschweig

Darrigol O. 2002. Between Hydrodynamics and Elasticity Theory: The First Five Births of the Navier-Stokes Equation. *Archive for History of Exact Sciences* **56**: 95-150

Darrigol O. 2003. Number and measure: Hermann von Helmholtz at the crossroads of mathematics, physics, and psychology. *Studies in History and Philosophy of Science* **34**: 515-573

Darrigol O. 2010. James MacCullagh's ether: An optical route to Maxwell's equations?, *The European Physical Journal H*, **35**: 133-172

Darrigol O. and J. Renn. 2003. La nascita della meccanica statistica. *Storia della Scienza,* Istituto della Enciclopedia Italiana, chapter xlv, pp. 496-507

Daub E.E. 1970. Entropy and Dissipation. *Historical Studies in the Physical Sciences* **2**: 321-354

Deltete R. 1999. Helm and Boltzmann: Energetics at the Lübeck Naturforscherversammlung. *Synthese* **119**: 45-68

Deltete R. 2000. Helm's history of energetics: a reading guide. in Helm G. 2000, pp. 4-45

Deltete R.J. 2012. Planck, Ostwald, and the Second Law of thermodynamics. *HOPOS* **2**: 121-146

Dugas R. 1937. La méthode physique au sens de Duhem devant la mécanique des quanta. *Revue générale des Sciences pures et appliquées* **48**: 68-71

Duhem P. 1886. *Le potentiel thermodynamique et ses applications à la mécanique chimique et à la théorie des phénomènes électriques*, Hermann, Paris

Duhem P. 1891. Sur les équations générales de la Thermodynamique. *Annales Scientifiques de l'Ecole Normale Supérieure*, 3^e série, tome **VIII**: 231

Duhem P. 1892. Commentaire aux principes de la Thermodynamique – Première partie, *Journal de Mathématiques pures et appliquées*, 4^e série, tome **VIII**: 269

Duhem P. 1894a. Commentaire aux principes de la Thermodynamique – Troisième partie, *Journal de Mathématiques pures et appliquées*, 4^e série, tome **X**: 203

Duhem P. 1894b. Sur les déformations permanentes et l'hystérésis. *Mémoires présentées par divers savants étrangères et Mémoires couronnées par l'Académie de Belgique*, Classe des Sciences, tome **LIV**: 1894

Duhem P. 1894c. Les théories de l'optique", *Revue des deux mondes* **123**: 94-125

Duhem P. 1895a. Sur les déformations permanentes et l'hystérésis – Deuxième mémoire: les modifications permanentes du soufre, *Mémoires présentées par divers savants étrangères et Mémoires couronnées par l'Académie de Belgique*, Classe des Sciences, tome **LIV**: 1895

Duhem P. 1895b. Sur les déformations permanentes et l'hystérésis – troisième mémoire: Théorie générale des modifications permanentes. *Mémoires présentées par divers savants étrangères et Mémoires couronnées par l'Académie de Belgique*, Classe des Sciences, tome **LIV**: 1895

Duhem P. 1896. *Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques*, Hermann, Paris

Duhem P. 2011, *Commentary on the Principles of thermodynamics by Pierre Duhem*, (Edited and Translated, with an Introduction by Paul Needham), Springer, Dordrecht, Heidelberg, London, New York

FitzGerald G.F. 1880. On the Electromagnetic Theory of the Reflection and Refraction of Light. *Philosophical Transactions of the Royal Society* **171**: 691-711

Gibbs J.W. 1875-8. On the Equilibrium of Heterogeneous Substances, *Transactions of the Connecticut Academy*, in *The Scientific Papers of J. Willard Gibbs*, *thermodynamics*, Longmans, Green and Company, New York, Vol. I, pp. 55-349

Gibbs J.W. 1889. Rudolf Julius Emanuel Clausius. *Proceedings of the American Academy*, 16, pp. 458-65; reprinted in Gibbs J.W. 1906 **2**:261-267

Gibbs J.W. 1906. *The Scientific Papers of J. Willard Gibbs*, Longmans, Green, and Co., London, New York, and Bombay

Gillispie C.C. (ed.), 1970-80, *Dictionary of Scientific Biography*, Charles Schreibner's Sons, New York

Hamilton W.R. 1834. On a General Method in Dynamics; .... *Philosophical Transactions of the Royal Society*, part II for 1834, pp. 247-308

Hankins T.L. 1980. *Sir William Rowan Hamilton*, The John Opkins University Press, Baltimore and London

Helm G. 1898. *Die Energetik nach ihrer geschichtlichen Entwicklung*, Verlag von Veit & Comp., Leipzig; reprinted in Helm G. 1981, *Die Energetik nach ihrer geschichtlichen Entwicklung*, Arno Press, New York; in Helm G. 2000, *The Historical Development of Energetics* (Translated, and with an Introductory Essay by R.J. Deltete), Kluwer Academic Publishers. Dordrecht, Boston, London

Helmholtz H. 1882. Die Thermodynamik Chemischer Vorgänge. *Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin*, (2 Febr. 1882) **I**: 22-39; in Helmholtz H. 1883, pp. 958-978

Helmholtz H. 1883. *Wissenschaftliche Abhandlungen*, II Band, Barth, Leipzig

Hertz H. 1894. *Die Prinzipien der Mechanik (In neuem Zusammenhange dagerstellt)*, Barth, Leipzig; English translation in Hertz H. 1956, *The Principles of mechanics*, Dover, New York

Hoffmann D. 2008. *Max Planck: Annalen Papers*, Wiley-VCH, Weinheim

Jaki S.L. 1984. *Uneasy Genius: the Life and Work of Pierre Duhem*, Martinus Nijhoff Publishers, The Hague

Jellet J. and S. Haughton (eds.) 1880. *The collected works of James MacCullagh*, Hodges, Figgis & Co., Dublin, Longmans, Green & Co., London

Jouguet E. 1908. *Lectures de Mécanique, Première partie – la naissance de la Mécanique*, Gauthier-Villars, Paris

Jouguet E. 1917. L'œuvre scientifique de Pierre Duhem. in *Revue générale des Sciences pures et appliquées*, Paris, pp. 40-49

Klein M.J. 1969. Gibbs on Clausius. *Historical Studies in the Physical Sciences* **1**: 127-149

Kragh H. 1993. Between physics and Chemistry: Helmholtz's Route to a Theory of Chemical thermodynamics. in Cahn D. (ed.) 1993, pp. 403-431

Kragh H. 2008a. *Entropic Creation – Religious Context of thermodynamics and Cosmology*, Ashgate, Farnham (England)

Kragh H. 2008b. Pierre Duhem, Entropy, and Christian Faith. *Physics in Perspective* **10**: 379-395

Kragh H. and S.J. Weininger. 1996. Sooner Silence than Confusion: The Tortuous Entry of Entropy into Chemistry. *Historical Studies in the Physical and Biological Sciences* **27**: 91-130

Kuhn T.S. 1987. *Black-Body Theory and the Quantum Discontinuity 1894-1912* (With a New Afterword), The University of Chicago Press, Chicago & London

Lagrange J.L. 1811. *Mécanique analytique*, tome premier, Courcier, Paris

Laidler K.J. 1993. *The World of Physical Chemistry.* Oxford University Press, Oxford, New York, Toronto

Lindsay R.B. 1937. Carl Barus: 1856-1935. *Proceedings of the American Academy of Arts and Sciences* **71**: 484-489

MacCullagh J. 1848 (read 9 Dic. 1839). An essay towards the dynamical theory of crystalline reflexion and refraction. in Jellet J. and Haughton S. 1880 (eds.), part 1, pp. 145-184

Massieu F. 1869a. Sur les Fonctions caractéristiques des divers fluides. *Comptes Rendus de l'Académie des Sciences* **LXIX**: 858-862

Massieu F. 1869b. Addition au précédent Mémoire sur les Fonctions caractéristiques", *Comptes Rendus de l'Académie des Sciences* **LXIX**: 1057-1061

Massieu F. 1876. Mémoire sur les Fonctions caractéristiques des divers fluides et sur la théorie des vapeurs. *Mémoires des Savants étrangers* twentiethII, pp. 1-92

Maxwell J.C. 1860. Illustrations of the Dynamical Theory of Gases; reprinted in Maxwell J.C. 1890 **1**: 377-409

Maxwell J.C. 1867. On the Dynamical Theory of Gases. *Philosophical Transactions London*, 157, pp. 49-88; reprinted in Maxwell J.C. 1890 **2**: 26-78

Maxwell J.C. 1878. Tait's *thermodynamics. Nature*, pp. 257-9; reprinted in Maxwell J.C. 1890 **2**: 660-71

Maxwell J.C. 1890. *The Scientific Papers of James Clerk Maxwell*, (Niven W.D. ed.), 2 vols, University Press, Cambridge

McCormmach R. and C. Jungnickel. 1986. *Intellectual Mastery of Nature*, 2 vols., The University of Chicago Press, Chicago, London

Miller D.G. 1967. Pierre Duhem, un oublié. *Revue des Questions Scientifiques*, 138 (Octobre 1967), pp. 445-70; it was the French translation of Miller D.G. 1966, Ignored Intellect: Pierre Duhem. *Physics Today* **19**: 47-53

Müller I. 2007. *A History of Thermo-dynamics. The Doctrine of Energy and Entropy*, Dover, New York

Müller I. and W. Weiss. 2012. Thermodynamics of irreversible processes – past and present. *The European Physical Journal H* **37**: 139-236

Needham P. 2011. Introduction; in Duhem P. 2011, pp. v-xi

Norton Wise M. 1982. The Maxwell Literature and the British Dynamical Theory. *Historical Studies in the Physical Sciences* **13**: 175-205

Oettingen A. 1885. Die thermodynamischen Beziehungen antithetisch entwickelt", *Mémoires de l'Académie impériale des Sciences de Saint-Pétersbourg*, Tome twentieth **XII**: 1-70

Oettingen A.J. 1876. Ueber Temperatur und Adiabate. *Annalen der Physik und Chemie, Ergänzungsband* **7**: 83-133

Ostwald W. 1896. Zur Energetik. *Annalen der Physik und Chemie* **58**: 154-167

Planck M. 1879. *Über der zweiten Hauptsatz der mechanischen Wärmetheorie*, Ackerman, Munich

Planck M. 1880. *Gleichgewichtszustände isotroper Körper in verschiedenen Temperaturen*, Theodore Ackermann, München

Planck M. 1882. Verdampfen, Schmelzen und Sublimieren. *Annalen der Physik und Chemie* **15**: 446-475

Planck M. 1889. A. von Oettingen. Die thermodynamischen Beziehungen antithetisch entwickelt. *Annalen der Physik* (Beiblätter), twentiethIII, pp. 466-9; reprinted in Hoffmann D. 2008, pp. 838-341

Planck M. 1893. *Grundriss der Allgemeinen Thermochemie*, Eduard Trewendt, Breslau

Planck M. 1897. *Vorlesungen über Thermodynamik*, Veit & Comp., Leipzig

Planck M. 1905. *Vorlesungen über Thermodynamik*, (zweite, verbesserte Auflage), Veit & Comp., Leipzig

Rankine W.J.M. 1851. On the Centrifugal Theory of Elasticity and its Connection with the Theory of Heat, in Rankine W.J.M. 1881, pp. 49-66.

Rankine W.J.M. 1853a. On the Mechanical Action of Heat, Section **VI**, in Rankine W.J.M. 1881, pp. 310-338

Rankine W.J.M. 1853b. On the General Law of the Transformation of Energy. in Rankine W.J.M. 1881, pp. 203-208

Rankine W.J.M. 1855. Outlines of the Science of Energetics". in Rankine W.J.M. 1881, pp. 209-228

Rankine W.J.M. 1881. *Miscellaneous Scientific Papers*. Charles Griffin and Company, London

Serrin J. (ed.) 1986. *New Perspectives in Thermodynamics*. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo

Servos J.W. 1990. *Physical Chemistry from Ostwald to Pauling*, Princeton University Press, Princeton

Stokes G.G. 1883. *Mathematical and Physical Papers*, vol. II, University Press, Cambridge

Tait P.G. 1877. *Sketch of thermodynamics*, second edition, David Douglas, Edinburgh

Tait P.G. 1880. Memoir. in Rankine W.J.M. 1881, pp. xix-xxxvi

Thomson J.J. 1888. *Applications of Dynamics to physics and Chemistry*, Macmillan and Co., London and New York

Timoshenko S.P. 1983. *History of Strength of Materials*, Dover, New York

Truesdell C. 1984. *Rational thermodynamics*. Springer-Verlag, New York, Berlin, Heidelberg, Tokyo

Truesdell C. 1986. What Did Gibbs and Carathéodory Leave Us About Thermodynamics?. in Serrin J. (ed.) 1986, pp. 101-124

Ugaglia M. 2004. *Modelli idrostatici del moto da Aristotele a Galileo*, Lateran University Press, Roma