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**Widening the Scope of Analytical Mechanics**

Duhem's third pathway to Thermodynamics



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“Or, la réalité est complexe, infiniment ; chaque perfectionnement nouveau des méthodes expérimentales, en scrutant plus profondément les faits, y découvre des nouvelles complications ; l’esprit humain, dans sa faiblesse, a beau s’efforcer vers une représentation simple du monde extérieur ; il lui suffit de placer l’image en face de l’objet et de comparer avec bonne foi pour constater que cette simplicité, si ardemment souhaitée, est une insaisissable chimère, une irréalisable utopie.”

(Duhem P. 1903, in Duhem P. 1992, pp. 342-3)

## Foreword

Much literature has been published on Duhem as a historian and philosopher of science, whereas much less is available on Duhem as a physicist. This sounds quite astonishing when we realize that he published an immense number of papers and books on theoretical physics. Pierre Duhem's theoretical physics has been less studied than his history and philosophy of science although his historical and philosophical researches were influenced by his practice as a theoretical physicist. For a long time, and even nowadays in the scientific community, Duhem's theoretical and meta-theoretical design has been a sort of buried memory. I hope that this preprint can fill the gap: I would like to cast some light on Duhem's design of unification between Mechanics and Thermodynamics, and between Physics and Chemistry. I will analyze the theoretical researches Duhem undertook in the last years of the nineteenth century, in particular from 1886 to 1896. The study of Duhem's physics is demanding, because both the conceptual and mathematical aspects of his theories are quite sophisticated. Some of the issues he raised, in particular the complexity of the physical world, did not attract his contemporaries. Only after some decades, in the second half of the twentieth century, complexity met the interest of physicists. Moreover, he revived the tradition of Aristotle's natural philosophy, a tradition which had been looked upon as regressive in the context of the history of science.<sup>1</sup>

When Duhem undertook his theoretical enterprise, Thermodynamics could rely on a meaningful history, and he considered himself as an upholder of a "third pathway" to Thermodynamics. According to Duhem, the first pathway corresponded to Thermodynamics as "an application of Dynamics", and the kinetic theory was at stake. Heat was interpreted as "a tiny and rapid motion of particles composing ordinary bodies", and temperature was identified with "the average living force corresponding to that motion". The second pathway corresponded to a phenomenological approach: Thermodynamics was based on "specific principles", and was "independent of any hypothesis on the nature of heat". Duhem's third pathway was based on "a different relationship between Dynamics and Thermodynamics": "Dynamics became a specific instance of Thermodynamics", and general principles encompassed "all kinds of transformations, from the change of place to the change of physical qualities".<sup>2</sup>

From 1886 onwards, Duhem pursued a theoretical design which consisted of two subsequent steps. He rephrased Thermodynamics consistently with the *language* of Analytical Mechanics, and conversely he founded Mechanics on the principles of Thermodynamics. He

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<sup>1</sup> Although biographies and studies on Duhem's history and philosophy of science have flourished in the last decades, studies on his physics are rare. Apart from the book published in 1927 by the physicist Octave Manville, I can only mention Paul Brouzeng's 1981 doctoral dissertation. Brouzeng considered Duhem as a "pioneer of thermodynamics of irreversible processes", and considered his theoretical researches as part of a "chain" connecting "Carnot to Prigogine" (Brouzeng P. 1981, vol. 1, pp. 73 and 157). Even in recent studies, Duhem's contribution to physics, in particular Thermodynamics, is underestimated or neglected. See, for instance, Uffink J. 2001, a penetrating and detailed reconstruction of the history of the second Principle of thermodynamics: see in particular Uffink J. 2001, pp. 15 and 389.

<sup>2</sup> See Duhem P. 1894a, pp. 284-5: "Nous avons essayé, dans le présent travail, d'indiquer une troisième position de la Dynamique par rapport à la Thermodynamique ; nous avons fait de la Dynamique un cas particulier de la Thermodynamique, ou plutôt, nous avons constitué, sous le nom de Thermodynamique, une science qui embrasse dans des principes communs tous les changements d'état des corps, aussi bien les changements de lieu que les changements de qualités physiques."

then tried to unify “local motion”, thermal phenomena, electromagnetic phenomena, and chemical transformations of matter in the framework of a generalized Mechanics.

Duhem was born in 1861, and his intellectual life was influenced by the birth of the Third French Republic, and the sharp political and cultural debates which followed it. He was educated in a conservative and catholic family. His wide interests and specific competences made it easy for him to enter the prestigious *École Normale Supérieure*, where he gained his “agrégation” in 1885. The previous year he had submitted a dissertation in mathematical physics on thermodynamic potentials. The dissertation was rebuffed, probably because he had criticised Marcelin Berthelot’s thermo-chemistry. Berthelot was a member of the political and academic establishment in France: an influential chemist with serious interests in the history of science, professor at the *Collège de France*, moderate republican, he was also a member of Parliament and minister. Subsequently, the academic and political influence exerted by Berthelot and his school forced Duhem to publish some books abroad, in particular in Belgium. Duhem’s second doctoral dissertation dealt with the thermodynamic interpretations of magnetic effects, and was accepted in the section of mathematics in 1888.<sup>3</sup> In 1887 he had been appointed “maître de conférences” to Lille university, where he spent six years: he taught physics, and published important papers and essays. In October 1890 he got married, and in September 1891 his daughter Hélène was born, but his wife died in July 1892. In 1893, after a bitter quarrel over the misuse of a laboratory in the course of an exam, he left Lille and went to Rennes University. In 1894 he was appointed to a chair of physics at Bordeaux University, where he taught and did research for the remaining part of his life as professor of theoretical physics. He did not managed to gain an academic position in Paris, but in 1913 he was elected “membre non résident” de l’Académie des sciences.<sup>4</sup>

He gave an impulse to physical chemistry, and was a pioneer of thermodynamics of irreversible processes, a field of physics which started to flourish only in the 1920s. He undertook very demanding researches on natural philosophy in the Middle Ages, and he claimed that, at the end of the XIII century, some Christian philosophers opened the way to modern science. He died suddenly in 1916. If his theoretical physics was underestimated by the scientific community in the course of his life, and was re-evaluated only around the middle of the twentieth century, his historical studies and philosophical remarks on science have had a greater influence: they have been enthusiastically appreciated but also sharply criticised.<sup>5</sup>

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<sup>3</sup> See Brouzeng P. 1981a, p. 147: “... ce fut, en fin de compte, un jury de mathématiciens qui lui conféra le titre de Docteur es Sciences mathématiques en 1888.” See also *Ibidem*, p. 44.

<sup>4</sup> Duhem was living in a period which was subsequently crossed by the fall of the Second Empire, the war against Prussia, the defeat, the insurgency of the Commune, the ideological struggles on the laicism of the state, and the Dreyfus case. For a survey of Duhem’s biography in the context of France political and cultural history, see Brouzeng P. 1987, pp. 11-81, and the volume Stanley Jaki devoted to Duhem’s life and scientific career (Jaki S.L. 1984). Some biographical information is found in most of the secondary literature mentioned in the Bibliography.

<sup>5</sup> In the late nineteenth century, physicists were more interested in atoms and new rays than in Duhem’s theories: moreover the latter never underwent dramatic corroborations. In France, he was more appreciated by mathematicians than by physicists and chemists. Only in German speaking countries and in the States his theories attracted the community of physical-chemists. See Brouzeng P. 1981a, pp. 62, 72, 152, and 272.



### *Thermodynamics and Complexity*

In 1979, in their famous book *La nouvelle alliance*, Prigogine and Stengers claimed that the first step towards the theory of complexity was undertaken in 1811, when Jean-Joseph Fourier won a prize from the *Académie des Sciences* with his *Théorie analytique de la chaleur*. A new mathematical physics was emerging besides Laplace's mechanics: the new science of heat opened a wider horizon, beyond the already explored *Newtonian* land. A wide class of phenomena, dealing with heat and the transfer of heat, required a different physical and mathematical approach: equations describing fluxes of new physical entities, instead of equations describing forces acting between couples of particles.<sup>6</sup>

In reality, no theory of complexity explicitly emerged at the beginning of the nineteenth century: only in a very broad sense can Fourier be considered the *father* of the theory of complexity. From the historical and the epistemological point of view, our concept of "complexity", or the concept of complexity which Prigogine and Stengers made reference to, emerged in the second half of the twentieth century, and cannot be traced back to the early nineteenth century. In order to uncover the roots of complexity in physics, the theoretical researches undertaken around the end of the nineteenth century in the field of Thermodynamics appear far more meaningful than Fourier's book. In particular, Duhem's theoretical contribution, at the end of that century, appears to me the most meaningful.

Since we are dealing here with complexity in the specific context of physics, I shall assume that complexity in a physical system involves some typical issues: the impossibility to reduce the system to the sum of its subsets, its sensitivity to initial conditions, and the existence of irreversible processes. In the debates on the foundations of thermodynamics, which took place at the end of the nineteenth century, initial conditions, irreversibility, and the relationship between microscopic elements of a system and the macroscopic system itself appeared mutually connected. In the last decades of that century, even theoretical models quite different from Duhem's, for instance the models of gases put forward by Maxwell and Boltzmann, let similar questions emerge. How could the time-irreversible behaviour of a macroscopic amount of gas be explained in terms of the time-reversible behaviour of microscopic molecules, which were its ultimate components?

However Prigogine and Stengers managed to catch the deep intrinsic novelty which thermodynamics introduced into physical sciences: if mechanical systems could experience different final states depending on the different initial states, thermodynamic systems seemed to drift towards a macroscopically indistinguishable state of equilibrium.<sup>7</sup> Nevertheless they underestimated Duhem's theoretical pathway, which led to a new generalized Mechanics. Following Duhem's *third pathway* we can fully appreciate one of the most outstanding

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<sup>6</sup> See Prigogine I. and Stengers I. 1986, pp. 166-7: "En ce qui concerne la science de la complexité, nous n'hésitons pas à la faire «commencer», en ce sens, dès 1811. En cette année, où les laplaciens triomphent et dominent la science européenne, le baron Jean-Joseph Fourier, préfet de l'Isère, remporte le prix de l'Académie pour son traitement théorique de la propagation de la chaleur dans les solides. [...] Le rêve laplacien, à l'heure de sa plus grande gloire, a subi un premier échec: une théorie physique existe désormais, mathématiquement aussi rigoureuse que les lois mécaniques du mouvement et absolument étrangère au monde newtonien; la physique mathématique et la science newtonienne ont cessé d'être synonymes."

<sup>7</sup> See Prigogine I. and Stengers I. 1986, p. 192: "Combien ce langage est étranger à celui de la dynamique! Là, le système évolue sur une trajectoire donnée une fois pour toutes, et garde éternellement le souvenir de son point de départ (puisque les conditions initiales déterminent une fois pour toutes la trajectoire). Ici, au contraire, *tous* les systèmes en état de non-équilibre évoluent vers le *même* état d'équilibre. Arrivé à l'équilibre, le système a *oublié* ses conditions initiales, a oublié la manière dont il a été préparé."

achievements of late nineteenth century theoretical physics: a new alliance between the formal structure of Analytical Mechanics and Thermodynamics, in order to deal with the complexity of the physical world. Here we find a kind of physics quite difficult to fit into any theoretical and meta-theoretical framework.

In the 1820s, Fourier had explicitly stated that “mechanical theories are not suitable for phenomena involving heat”, and that a new theory, “not less rigorously founded” than mechanics, was required. In the same years, a French engineer, S. Carnot, inquiring into the relationship between mechanical and thermal processes in thermal engines, found a precise law ruling the transformations of caloric transfer into mechanical work.<sup>8</sup> In the 1850s, a young Scottish natural philosopher, W. Thomson, tried to integrate a principle of conservation of energy with Carnot’s theory of thermal engines. Moreover, he tried a cosmological extrapolation, and imagined a Universe running towards its death because of the waste of heat, both in spontaneous transformations and in thermal engines. In 1852, Thomson’s key-concept became “dissipation”: although conserved, energy underwent a sort of degradation, because of irreversible processes. In some papers published since the 1850s, Clausius abandoned Carnot’s idea that heat was conserved, and put forward different versions of a fundamental law which was soon known as the second law of thermodynamics. He introduced a new physical concept, “the content of transformation”, which was conserved in ideal thermal engines. Subsequently he introduced the concept of *entropy*, a state function whose value could not decrease.<sup>9</sup>

Those papers captured the interest of Maxwell; in the 1860s, he made use of statistical concepts in order to obtain the distribution of molecular velocities in a gas. In the 1870s, L. Boltzmann attempted to develop a statistical theory of entropy. The most important novelty was the introduction of probability in physics: probability became an intrinsic feature of physical systems with a huge number of elementary components. Boltzmann tried to go far beyond Maxwell: he was not satisfied with the description of the state of equilibrium. In 1872, he looked for a law which could also describe the evolution towards that equilibrium. He was strongly influenced by Darwin’s researches on biological evolution. He imagined a law of evolution which did not involve the single molecule, or its individual path, but the whole system of molecules. From 1877 onwards, statistics and probability did not represent a

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<sup>8</sup> Fourier’s treatise was a new version, published in 1822, of his 1811 essay. See Fourier J. 1822, pp. ii-iii: “Mais quelle que soit l’étendue des théories mécaniques, elles ne s’appliquent point aux effets de la chaleur. Ils composent un ordre spécial de phénomènes qui ne peuvent s’expliquer par les principes du mouvement et de l’équilibre.”. See also p. xi: “Les équations différentielles de la propagation de la chaleur expriment les conditions les plus générales, et ramènent les questions physiques à des problèmes d’analyse pure, ce qui est proprement l’objet de la théorie. Elles ne sont pas moins rigoureusement démontrées que les équations générales de l’équilibre et du mouvement.” See Carnot S. 1824, in Carnot S. 1878, pp. 6-7: “La production de la puissance motrice est donc due, dans les machines à vapeur, non à une consommation réelle du calorique, *mais à son transport d’un corps chaud à un corps froid*, c’est-à-dire à son rétablissement d’équilibre ... Nous verrons bientôt que ce principe est applicable à toute machine mise en mouvement par la chaleur. D’après ce principe, il ne suffit pas, pour donner naissance à la puissance motrice, de produire de la chaleur : il faut encore se procurer du froid ; sans lui, la chaleur sera inutile. [...] Partout où il existe une différence de température, partout où il peut y avoir rétablissement d’équilibre du calorique, il peut y avoir aussi production de puissance motrice.”

<sup>9</sup> See chapter 1 in the present preprint. A historical reconstruction of this stage of Thermodynamics can also be found in Duhem P. 1895c, pp. 401-18. A more recent history can be found in Brush S.G. 1976, book 2, pp. 568-71. Apart from the obvious time lag between their historical researches, two different histories of Thermodynamics emerge from their studies, even though they have in common the fact of being both physicists and historians.

sort of contrivance but the suitable intellectual tool to describe the evolution of a great population of molecules.<sup>10</sup>

Both Maxwell and Boltzmann pointed out the statistical meaning of the second law: that law could be locally violated, even though it preserved its validity on the large scale of space and time. The new, complex interplay between Mechanics and Thermodynamics raised a widespread debate, well-known to historians of physics.<sup>11</sup>

A different theoretical pathway was undertaken by the Scottish engineer William J.M. Rankine, and by the French engineer Robert Massieu: they tried a highly abstract, mathematical interpretation of Thermodynamics. If the role of the former in the history of Thermodynamics has been acknowledged by contemporary physicists and by present-day historians, the latter is less known. Rankine put forward an abstract re-interpretation of Thermodynamics, and tried to extend the new formal framework to all fields of physics, giving rise to a wide design of unification he labelled “Energetics”. Massieu was a mining engineer and professor at Rennes university: he was able to demonstrate that some mechanical and thermal properties of physical and chemical systems could be derived from two “characteristic functions”.<sup>12</sup>

Josiah W. Gibbs and Hermann von Helmholtz developed that abstract re-interpretation of Thermodynamics, and exploited the structural analogy between Mechanics and Thermodynamics. Between 1875 and 1879, in the series of papers under the common title “On the Equilibrium of the Heterogeneous Substances”, Gibbs showed that Massieu functions played the role of potentials. In particular, the two functions were nothing else but the thermodynamic potential at constant temperature and volume, and the thermodynamic potential at constant temperature and pressure. In 1883 Helmholtz introduced the concept of “free energy”: it was the variation of free energy, rather than the whole delivery of heat, which allowed scientists to predict the actual direction of chemical transformations.<sup>13</sup>

In 1886, Duhem published *Le potentiel thermodynamique et ses applications à la mécanique chimique et à la théorie des phénomènes électriques*, where he showed that the entropy and volume of a physical system corresponded to some derivative of a thermodynamic potential. Other derivatives allowed him to obtain coefficients of dilatation and compressibility, as well as specific heat at constant pressure. In 1891, in the essay “Equations générales de la Thermodynamique”, he generalized the concept of “virtual work” under the action of “external actions” by taking into account both mechanical and thermal actions. In 1894 the design of a generalized Mechanics based on thermodynamics was further

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<sup>10</sup> On Boltzmann evolutionism see Boltzmann L. 1892, in Boltzmann L. 1974, pp. 7-11, Boltzmann 1899, pp. 79-80, and Boltzmann L. 1905, pp. 592-5. This stage of the history of Thermodynamics is discussed, for instance, in Duhem P. 1895c, pp. 424 and 434-5, and more widely in Brush S.G. 1976, book 1, chapters 4, 5 and 6.

<sup>11</sup> The criticism about Boltzmann theory, in particular Loschmidt’s criticism, Zermelo’s criticism, and the debate between Boltzmann and British physicists, is discussed in Dugas R. 1959, pp. 160, 180, 207-8, and 212-3. See also Brush S. 1976, book 1, pp. 96 and 239, and Brush S. 1976, book 2, pp. 356-63.

<sup>12</sup> See chapter 2 in the present preprint. Although mentioned by Josiah W. Gibbs and Duhem, the name of “Massieu” does not appear in the *Dictionary of Scientific Biography*, nor in the recent supplement. He is mentioned in Klein M.J. 1983, p. 161, footnote 35, and Kragh H. 1993, pp. 403-31. The “Massieu functions” are mentioned in some books on statistical mechanics and thermodynamics. See Callen H. 1985, sections 5.4 and 6.7. See also Balian R. 1992, § 5.6, and Perrot P. 1998, p. 190.

<sup>13</sup> See chapter 2 in the present preprint.

developed: ordinary mechanics had already become “a particular case of a more general science”.<sup>14</sup>

In 1896, in the very long essay “Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques”, he proceeded to make a detailed reconstruction of some physical and chemical processes neglected or underestimated by physicists because of their complexity. In the equations of his generalized Mechanics-Thermodynamics, some new terms had to be introduced, in order to account for the intrinsic *viscosity* and *friction* of the system. In the meanwhile, starting from 1895, he had begun to develop a theory which took into account the permanent modifications of bodies, in a series of essays under the common title “Les déformations permanentes et l’hysteresis”. This ambitious design was hindered by many difficulties, both theoretical and experimental.<sup>15</sup>

Two reasons have led me to focus on the decade 1886-1896. In the first place, I have found that Duhem’s pathway was substantially accomplished before the turn of the century. Even Duhem’s meta-theoretical remarks, which he expressed in a systematic way in his 1906 *La théorie physique, son objet, et sa structure*, stemmed from his practice as a theoretical physicist in those years. In second place, I would like to stress that those remarks were put forward before the transformations experienced by the physical sciences around the turn of the century. Not only am I referring here to Planck’s hypothesis of quanta or Einstein’s re-interpretation of mechanics and electromagnetism, but also to experimental and theoretical researches on the new rays and the new particles.<sup>16</sup>

Galileo’s modern science had had to fight against the old physics of qualities, in order to establish itself. The complexity of the physical world had been neglected in favour of a simplified representation: only geometry and mechanics could explain a geometrized and mechanized world. Duhem believed that, at the end of the nineteenth century, he could go back to that neglected phenomena, and carry it into the wider boundaries of a generalized Mechanics-Thermodynamics. He revived the ancient Greek meaning of the word “physics”: not only the science of local motion, but a general theory of material transformations, which encompassed Physics, Chemistry and perhaps some aspects of life sciences. Only a new kind of physics, a generalized physics indeed, could describe the complexity of the physical world.<sup>17</sup>

Duhem neither underrated nor refused the seventeenth-century scientific revolution; he did not try to turn back, in order to take shelter in ancient philosophies. He aimed at widening the scope of physics: the new physics could not confine itself to “*local motion*” but had to describe what Duhem qualified “*motions of modification*”. Some processes, which had been called “*generation and corruption*” in peripatetic words, could be labelled “*chemical reactions*” in contemporary words. It is worth mentioning that Duhem’s great design of

<sup>14</sup> See chapters 3 and 4 in the present preprint. See also Duhem P. 1886, pp. 11-13, and Duhem P. 1894a, p. 285.

<sup>15</sup> See chapter 5 in the present preprint. See also Duhem P. 1896, p. 205.

<sup>16</sup> Roberto Maiocchi made a similar remark some decades ago. See Maiocchi R. 1985, p. 132: “... la sua riflessione epistemologica era giunta a risultati mature già nel 1894, prima ancora della semplice scoperta sperimentale della radioattività e non risulta in alcun modo collegata alle grandi rivoluzioni fisiche del novecento.”

<sup>17</sup> See Duhem P. 1896, p. 205: « ... les divers changements de propriétés d’un système ne se réduisent pas au mouvement local; une même science doit réunir en ses principes à la fois les lois du mouvement local et les lois selon lesquelles se transforment les qualités des corps. » See also p. 206: « On est alors conduit à se demander s’il n’y a pas lieu d’appliquer aux tissus vivants une thermodynamique nouvelle; ... »

unification opposed Boltzmann's theoretical design. If Boltzmann had tried to proceed from "local motion" to attain the explanation of more complex transformations, Duhem was trying to proceed from general laws concerning general transformation in order to reach "local motion" as a simplified specific case.<sup>18</sup>

### *Thermodynamics in the Context of Theoretical Physics*

In the next chapters I will inquire into the network of general hypotheses, specific models and mathematical tools which emerged in the last decades of the nineteenth century and which found its more sophisticated expression in the texts of some outstanding natural philosophers and physicists: Maxwell, Boltzmann, Rankine, Gibbs, ... apart from Duhem himself. I have qualified them in a twofold way, as natural philosophers and physicists, for some specific reasons. Physics as a definite field of knowledge, a definite academic training, and a definite profession, was the outcome of a historical process which was accomplished in the second half of the nineteenth century. Until the first years of the twentieth century physics was practiced by scholars who belonged to various academic categories: mathematicians, physicists, engineers, and natural philosophers. If the emergence of physics as a definite academic discipline was a heritage of the late nineteenth century, the emergence of theoretical physics was the most interesting outcome of that process. Late nineteenth century theoretical physics stemmed from the fruitful alliance between the tradition of mathematical physics and the most speculative side of the tradition of natural philosophy.<sup>19</sup>

The analysis of that historical process is a very demanding task, because both cultural transformations and institutional events were involved. The academic recognition of theoretical physics was first achieved in German-speaking countries, although in a very contradictory way, but theoretical physics as an actual new practice in physics also appeared in France, Great Britain and then in Italy. We can mention Duhem and Henri Poincaré in France, Heinrich Hertz, Max Planck and Boltzmann in German-speaking countries, Joseph John Thomson and Joseph Larmor in the British Isles, and Vito Volterra in Italy. Some of them had been trained as mathematicians, and some others were engineers. From the academic point of view, Poincaré and Volterra were mathematicians. J.J. Thomson and Larmor had passed the highly selective Cambridge Mathematical Tripos, even though J.J. Thomson had gained his first degree as an engineer. We cannot forget that, among the first physicists who built up theoretical thermodynamics, Rankine and Massieu had been trained as engineers, and held chairs of engineering in Scotland and France respectively. Gibbs had also been trained as an engineer in the States, before undertaking his scientific specialisation in Europe. Duhem considered himself a physicist and a mathematician: after the rejection of his

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<sup>18</sup> See Duhem P. 1903, in Duhem P. 1992, pp. 199 and 218-9.

<sup>19</sup> On the process of specialization and professionalization taking place at the end of the nineteenth century, see, for instance, Ross S. 1964, p. 66, and Morus I.R. 2005, pp. 3, 6-7, 20, and 53. In Italy and Great Britain physics was also practiced by scholars appointed to the chairs of mathematics. Until the end of the nineteenth century, at Cambridge and in Scottish universities, high mathematical physics was practised by scholars who held chairs of mathematics or natural philosophy. On the emergence of theoretical physics at the end of the nineteenth century, see McCormach R. and Jungnickel C. 1986, vol. 2, pp. 33, 41-3, 48, and 55-6, and Bordoni S. 2008, pp. 35-45. On the concept of theoretical physics, see Boltzmann L. 1892, in Boltzmann L. 1974, pp. 5-11, and Boltzmann L. 1899, in Boltzmann L. 1974, p. 95.

first doctoral dissertation, the new one was accepted in the section of mathematics, and his physics was appreciated by mathematicians rather than by physicists.<sup>20</sup>

The hallmark of theoretical physics was the awareness that the alliance between the mathematical language and the experimental practice celebrated by Galileo had to be updated. Besides “definite demonstrations” and “sound experiments” there was a third component, which we could label conceptual or theoretical: it dealt with principles, models, and patterns of explanation. That conceptual component, neither formal nor empirical, was looked upon as a fundamental component of scientific practice. Different theories could share the same mathematical framework and make reference to the same kind of experiments: the difference among them could be found just at the conceptual level. Conversely, a given set of phenomena could be consistently described by different theories.<sup>21</sup>

Before the so-called Scientific Revolution, two intellectual traditions crossed the field of natural sciences: mathematics and natural philosophy. As Kuhn pointed out some decades ago, what nowadays we call “astronomy, statics, and optics” belonged to the tradition of mathematics: they required specialised practices and languages, and “practitioners” could rely on “bodies of literature directed exclusively” to them. The body of knowledge dealing with other natural phenomena, “like heat and electricity”, were within the scope of natural philosophy: in general, philosophical speculations on those subjects did not exclude some kinds of practical observation or experience. If the motion of celestial bodies was studied in the context of mathematics, local motions, namely motion on the Earth’s surface, were studied in the context of natural philosophy. Kuhn’s historical picture did not exclude some kind of communication between the two traditions, as for instance the mathematical analysis of local motion, which was undertaken by some fourteen-century scholars in Paris and Oxford.<sup>22</sup>

In some way, the distinction between the two traditions survived far into the nineteenth century, even though the processes that are sometimes qualified as Scientific Revolution led to a meaningful integration between the two fields. Indeed those processes involved a threefold alliance among the tradition of mathematics, the tradition of practical *arts*, and the tradition of natural philosophy. Both the speculative and empirical sides of natural philosophy underwent deep transformations: while Descartes put forward a new theoretical representation of the physical world, skilful British experimenters marked the passage from the practice of making experiences to the practice of making experiments. During the nineteenth century, the mathematisation of what Kuhn called “Baconian sciences” or “Baconian fields” corresponded to a new implementation of the alliance between natural philosophy and mathematics. Starting from 1811, Fourier put forward a sophisticated mathematical theory of some thermal phenomena, and starting from 1821, Ampère put forward a detailed mathematical theory of electrodynamical effects. Shortly before, a new kind of abstract and highly mathematised

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<sup>20</sup> It is worth mentioning that, in 1898, the mathematical physicist Georg Helm classified Clausius as “an outstanding representative of theoretical physics” (“ein hervorragender Vertreter theoretischer Physik”). See Helm G. 2000, p. 383 (Helm G. 1898, p. 343).

<sup>21</sup> It seems to me that a similar point of view has been put forward in Giannetto E. 1995, pp. 165-6, Kragh H. 1996, p. 162, and Lacki J. 2007, p. 248. For a historical reconstruction from the point of view of an early twentieth-century scholar, see Merz J.T. 1912, p. 199.

<sup>22</sup> Kuhn T.S. 1976, pp. 5 and 8.

physics had emerged: at the end of the eighteenth century, Lagrange had built up Analytical Mechanics, which had overtaken any reference to empirical entities.<sup>23</sup>

In the last decades of the nineteenth century, in the context of an accomplished mathematisation of *Baconian* sciences a further implementation of the alliance between mathematical physics and natural philosophy emerged: it was theoretical physics. Besides the integration between the recent tradition of Analytical Mechanics and the new theories of heat and electricity, theoretical physics realized a more sophisticated integration between a now wider-scope mathematical physics and the most speculative side of the long-lasting tradition of natural philosophy.

We have many instances of that widening of horizon in physics. An early instance was offered by Rankine's design of abstract generalisation of Thermodynamics. In the last decades of the century, in Larmor's theories we find the unifying role played by an invisible entity like aether. In Poincaré we find the legitimation of multiple theoretical approaches to a given set of phenomena. We also find Duhem's subtle interplay between mathematical, empirical, conceptual, historical and methodological aspects. What all these physicists had in common was a sophisticated methodology of scientific practice: there was an original combination of confidence and disenchantment with regard to science.<sup>24</sup>

The emergence of theoretical physics also corresponded to a new sensitivity to meta-theoretical issues: we find explicit designs of unification, explicit methodological remarks, and explicit debates on the foundations of physics. In that season, all these cogitations were looked upon as intrinsic aspects of scientific practice. Scientists did not entrust philosophers with reflections on aims and methods of science: meta-theoretical remarks emerged from the actual scientific practice, as a sort of new awareness.<sup>25</sup>

With regard to meta-theoretical debates, two different models of scientific knowledge were at stake. On the one hand, we find the attempt to go beyond the shield of visible phenomena, in order to catch their true microscopic nature. On the other hand, we find mathematical representations, without any attempt to pursue subtler explanations. We find the British Larmor, J.J. Thomson, George F. FitzGerald and Oliver Lodge, but also Hendrik A. Lorentz and Boltzmann deployed on the first front. On the second front we find Gustav Kirchhoff, Ernst Mach, and the *energetists* Georg Helm and Wilhelm Ostwald. Among those who swung from one to the other meta-theoretical options we find Hertz and then Planck: they followed Rankine, Maxwell, Clausius and Helmholtz's similar attitude. The debates involved Helm

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<sup>23</sup> Kuhn labelled "Baconian sciences" that field of natural philosophy which dealt with heat, electricity, magnetism, and other sets of phenomena where experimental investigations had actively been pursued in the decades which followed the so-called Scientific revolution, although no systematic mathematical theory had put forward. See Kuhn T.S. 1976, pp. 10-13. For some reference to British experimenters, see Kuhn T.S. 1976, p. 12.

<sup>24</sup> See, for instance, Boltzmann L. 1890, in Boltzmann L. 1974, pp. 33 and 35-6, Poincaré H. 1889, pp. II, III, and 2, Poincaré H. 1890, pp. VIII, and XIV-XV, Poincaré H. 1892, pp. XIV, and Larmor J. 1897, pp. 207 and 215.

<sup>25</sup> See Cassirer E. 1950, pp. 83-4: "Now not only does the picture of nature show new features, but the view of what a natural science can and should be and the problems and aims it must set itself undergoes more and more radical transformation. In no earlier period do we meet such extensive argument over the very conception of physics, and in none is the debate so acrimonious. [...] When Mach or Planck, Boltzmann or Ostwald, Poincaré or Duhem are asked what a physical theory is and what it can accomplish we receive not only different but contradictory answers, and it is clear that we are witnessing more than a change in the purpose and intent of investigation."

against Planck, and FitzGerald against Ostwald.<sup>26</sup> Poincaré looked on the two complementary attitudes with Olympian detachment. Boltzmann, Poincaré and Duhem clearly described the two meta-theoretical attitudes: *explanations* by means of specific mechanical models on the one hand, or *descriptions* by means of a formal language on the other. Although Duhem spoke against the mechanical models intensely exploited by British physicists, the role of theory and meta-theory was so important in his actual scientific practice that we cannot put him beside Mach, Helm or Ostwald without some specifications on their *Energetism* and their struggle against *Mechanism*.

At the end of the nineteenth century, the emergence of theoretical physics was only one aspect of a wider transformation in the field of physical sciences. From the 1860s onwards, physics had experienced two important transformations: in simplified terms, we could say that the first was internal and the second external to scientific practice. The former consisted in the systematisation of previous mathematical researches on heat and electricity. The latter consisted in the social success of science, which stemmed from recent technological achievements. Science had finally managed to realize, at least in part, Bacon's dream, and the myth of scientific progress emerged.<sup>27</sup>

We should analyse the two transformations separately. With regard to *internal* transformations, the second law of Thermodynamics and the concept of entropy let "the distinction between reversible and irreversible processes" emerge as "a basic feature in all natural events", as Cassirer remarked more than a half century ago. At the same time, "the Faraday-Maxwell field concept ... stood in sharp contrast at the outset with the Newtonian idea of force". In other words, the new concepts of "electromagnetic field" and "entropy" challenged the explanatory power of the mechanical representations of the physical world.<sup>28</sup>

With regard to *external* transformations, the last decades of the nineteenth century saw the spread of electromagnetic technologies, which really managed to improve the everyday life of ordinary people. Not only did electric light inside houses and on town roadsides modify the landscape of urban life, but it supplied a cleaner source of energy. Electric energy appeared as a healthy kind of energy when compared to oil or gas lamps. The advantages of electric energy consisted also in its versatility and portability: from the end of the 1860s, the world, mountains and oceans included, was crossed by a hundred thousand miles of telegraph cables. It was in that social and technological context that the myth of scientific progress emerged.

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<sup>26</sup> In Germany the debate was quite sharp, mainly in 1895, at the annual conference of German scientists and physicians held in Lübeck. On the importance of the Lübeck meeting as a "critical turning point in the fortunes" of Energetics, and on the different meta-theoretical attitudes of Helm and Ostwald, see Deltete R. 1999, p. 45. In a book published in 1898, Georg Helm pointed out the relevant features of a radical energetism. The debate continued after the conference, through the pages of *Annalen der Physik*, in 1895 and 1896. See McCormach R. and Jungnickel C. 1986, vol. 2, pp. 219-20, Cassirer E. 1950, pp. 96-7, and Harman P.M. 1982, pp. 147-8. For the points of view of the characters involved, see Ostwald W. 1896, Boltzmann L. 1896, Planck M. 1896, Helm G. 1895, and Helm G. 1898, p. 362 (English edition: Helm G. 1992, p. 401) For FitzGerald defence of specific theoretical models against Ostwald energetism, see FitzGerald G.F. 1896, pp. 441-2.

<sup>27</sup> We could say that, in Kuhn's terms, there was some kind of revolution, even though no physicist was then claiming that he was making a revolution. Kuhn's historiographical theses are too well-known to be discussed here. See, for instance, Kuhn T.S. 1996, 92-135. I remind the reader that, according to I.B. Cohen, we should not state that there was a revolution. On his four criteria for a revolution, see Cohen I.B. 1985, chapter II.

<sup>28</sup> See Cassirer E. 1950, p. 85. The concept has been recently revived by Renn J. and Rauchhaupt U. 2005, pp. 31-2.



As a consequence, a great expectation also emerged: scientific progress could trigger off a more general social progress.<sup>29</sup>

Duhem's awareness of the complexity of the physical world, as well as his awareness of the complexity of scientific enterprise, also emerged in that scientific and social context. Duhem's theories and meta-theoretical remarks represent a meaningful instance of late nineteenth-century theoretical physics, and an interesting instance of intellectual *progress*. Cultural transformations and scientific achievements which took place in the late nineteenth century represent the starting point of a long time-span which has lasted until our days. I find that the unearthing of the buried memory of Duhem's theoretical physics can cast some light on a *long century*, and on its twilight, which we now witness directly.<sup>30</sup>

### *Beyond Duhem's Theoretical Physics*

Both historians and philosophers of science have made use of scholarly labels in order to describe Duhem's scientific heritage: are they suitable labels, or merely "consolations for specialists"?<sup>31</sup> With regard to the label *energetism*, Duhem gave it the meaning of generalized Thermodynamics, rather than the meaning of a world-view or general meta-theoretical commitment in favour of the concept of energy. We find a remarkable conceptual distance between Duhem and some upholders of *energetics* like Helm and Ostwald. If Duhem developed a sophisticated mathematical theory of thermodynamics, Ostwald developed a physical world-view wherein "the concept of matter, which has become indefinite and contradictory, has to be replaced by the concept of energy". In no way can the name of Duhem be associated to that kind of *energetism*.<sup>32</sup>

With regard to the label *mechanism*, Duhem did not appreciate mechanical models, but relied on the structural analogy between Analytical Mechanics and Thermodynamics. He tried to build up a sophisticated abstract Mechanics, quite different from the mechanical models of British physicists. His theories could be qualified as a sort of *structural* mechanism: they were quite similar to Rankine's Energetics, where a generalised Mechanics merged with a generalised Thermodynamics.

He refused to make use of specific mechanical models of heat but, at the same time, made recourse to mechanical analogies in order to describe other scientific phenomena. An instance of these analogies can be found in Duhem's analysis of chemical "false equilibrium", which were associated to a motion along an inclined plane with friction. Duhem tried to found all

<sup>29</sup> With regard to the awareness of the scientific progress in the words of contemporaries, see Lami E.O. (ed.) 1881-91, *Supplement*, 1891, pp. 743. For a recent analysis, see Galison P. 2003, pp. 174-80.

<sup>30</sup> In Eric Hobsbawm's massive and authoritative book on the history of the twentieth century, *The Age of Extremes*, there are 65 occurrences of the expression "the Short Twentieth Century". I find that the cultural and social events which occurred in the twentieth century are deeply rooted in the late nineteenth century. In brief, I find that we are dealing with a sort of *Long Century*, which has spanned from the last decades of the nineteenth to the first years of the twenty-first century. (It was at the end of the nineteenth century that many kinds of *-isms* emerged and branched: among them we find the propagation of scientism.)

<sup>31</sup> I am referring to the title of Feyerabend's famous essay (Feyerabend P.K. 1970).

<sup>32</sup> See Ostwald W. 1896, pp. 159-60. According to Anastasios Brenner, Ostwald's energetism represented a sort of "disproportional" answer to atomism (Brenner A. 1990, pp. 82 and 86). It is worth mentioning that, in the 1960s, the scientist Donald G. Miller wrote that Duhem "belonged to the community of energetists, together with Ernst Mach, Georg Helm, and Wilhelm Ostwald". See Miller D.G. 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 P. 1981, vol. 2, pp. 226-8.

physics on the two principles of Thermodynamics but, at the same time, translated thermodynamics into the language of Analytical Mechanics. We could say that we find in Duhem both a mechanical foundation of thermodynamics and a thermodynamic foundation of mechanics.<sup>33</sup>

Even though I am focusing on Duhem's physics, I am aware that theoretical physics, the history of physics, and meta-theoretical reflections were mutually interconnected in Duhem's actual praxis. His design of re-interpretation of Aristotelian physics could be pursued only by a scientist endowed with a deep mastery of physics, a wide knowledge of history, and a subtle meta-theoretical sensitivity. It is worth remarking that his holism and his revised Aristotelism were deeply rooted in his researches in theoretical physics.<sup>34</sup>

Duhem had a dynamical and pliable conception of science, which has always poked fun at historians and philosophers who have tried to classify it. It is worth mentioning that his meta-theoretical remarks had much in common with Boltzmann's, a physicist who undertook an opposite pathway to Thermodynamics. Boltzmann's route to Thermodynamics through discontinuous and microscopic mechanical models was far from Duhem's route, which aimed at an abstract generalisation. At the same time, Boltzmann held a historical and evolutionary conception of science. Theoretical differences and meta-theoretical similarities between Duhem and Boltzmann can be properly appreciated if we carefully disentangle the level of specific physical theories from the level of meta-theoretical commitments.<sup>35</sup>

Duhem had kept together what subsequently scholars split into two different subject matters, namely history and philosophy of science.<sup>36</sup> Even though the present preprint does not deal with Duhem's philosophical, theological, and political commitments in a strict sense, I cannot exempt myself from reminding the reader that these issues have been widely studied and debated by scholars. If we read the considerable amount of secondary literature which has stratified in the course of ninety years, a wide range of contradictory appraisals emerges. In 1941 Armand Lowinger qualified Duhem's epistemology as "methodological positivism", in 1989 Bas van Fraassen qualified him as "an empiricist hero". In 2002 Jean-Francois Stoffel qualified Duhem as a phenomenalist, and after having carefully explained the difference

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<sup>33</sup> See Duhem P. 1896, p. 8: "Les faux équilibres que l'on rencontre en mécanique chimique ont leurs analogues parmi les équilibres purement mécaniques." The analogy is developed in *Ibidem*, pp. 8-9.

<sup>34</sup> The historical and epistemological remarks he had begun to publish systematically in the 1890s were subsequently collected in the book he published in 1906, *La théorie physique, son objet, et sa structure*. In the time interval we are interested in, Duhem published important papers on history and philosophy of science in the Belgian journal *Revue des questions scientifiques*. See Duhem P. 1892b, 1893c, 1893d, 1893e, 1894c, 1896b. See Stoffel J-F. 2002, p. 223: "L'histoire des sciences – et c'est là la grande originalité de notre auteur – fait donc partie intégrante du métier de physicien : ... [...] En étudiant l'histoire des théories physiques, Duhem n'a donc pas cessé d'œuvrer pour son projet scientifique."

<sup>35</sup> Boltzmann thought that theoretical physics dealt with "certain disputed questions which existed from the beginning", and which "will live as long as the science". Physical theories could not be looked upon as "incontrovertibly established truths": they were based on hypotheses which "require and are capable of continuous development". See Boltzmann L. 1905, pp. 592-5. I find that some epistemological analogies between Duhem and Boltzmann are at least as meaningful as those which Maiocchi found between Duhem and Poincaré, Mach or Hertz. See Maiocchi R. 1985, pp. 293-344.

<sup>36</sup> See Brenner A. 2011, pp. 1-3. It is true that, in the second half of the twentieth century, some "post-positivists called on Duhem's arguments and historical studies", but they "were pursuing their agenda". I find that Duhem's alliance between philosophy and history of science probably explains an "intriguing" fact: "after having inspired logical empiricists", Duhem's "ideas were taken up by their critics".

between “phenomenism” and “phenomenalism”, concluded that “he was realist in his heart, but phenomenalist in his mind”. In 2011, Paul Needham credited Duhem with “moderate realism”.<sup>37</sup> In 1922, the neo-Thomist François Mentré published a long paper in the neo-Thomist *Revue de philosophie*, in order “to pay homage to Pierre Duhem”, but qualified Duhem’s philosophy as “disappointing” and “ambiguous”: although quite sophisticated and essentially correct, “his religious philosophy” was considered essentially “defensive”. In 1979, Harry W. Paul remarked that, “[a]lthough Duhem is usually classified as a Thomist, his views were savagely contested by the hard-line Thomists”, who could not find in Duhem “the aggressive philosophy needed for modern Catholicism”. If in 1985, Roberto Maiocchi found that Duhem was isolated because of his “intermediate position between neo-Thomism and modernism”, in 1987, the physicist and historian of physics Stanley Jaki labelled Duhem a naive neo-Thomist: in his words, “Duhem’s Thomism was that of a passionately independent amateur”.<sup>38</sup>

It is worth remarking that, in the last decades of the nineteenth century, a wide debate on the relationship between science and theology took place, and the second Principle of Thermodynamics played an important role in it. Duhem did not appreciate the cosmological interpretations of the two Principles of Thermodynamics, and theological arguments based on them. He was a firm believer and, at the same time, “an independent mind”: he disliked transforming scientific contents into apologetic arguments, and always insisted on “a sharp separation between science and faith”.<sup>39</sup>

In the context of the late nineteenth-century cultural climate, wherein some philosophies courted recent scientific theories, Duhem insisted in keeping separate the two fields. He managed to catch the fruitfulness of some aspects of Aristotle’s theory of knowledge and natural philosophy, and at the same time, he refused to get involved in the revival of neo-Thomism.

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<sup>37</sup> See Lowinger A. 1941, in Lowinger A. 1967, p. 19, van Fraassen B. 1989, p. 353, fn. 2, Stoffel J.F. 2002, pp. 17, 24, 27, 47, and 367, and Needham P. 2011, p. 7. Even more astonishing are the appraisals given on Duhem’s political leanings, many decades ago. If in 1932, the mathematician Pierre Humbert claimed that Duhem was a democrat, in 1967, the scientist Donald G. Miller, who was sympathetic to Duhem’s scientific enterprise, qualified him as a “man of right, royalist, anti-Semitic, and extremist in religion”: in no way will I try to cast more light on these sensitive issues. See Humbert P. 1932, pp. 126, fn. 1, and pp. 133-4, and Miller D.G. 1967, pp. 463 and 468.

<sup>38</sup> See Mentré F. 1922, p. 460, Paul H.W. 1979, pp. 3 and 159, Maiocchi R. 1985, p. 13, and Jaki S.L. 1987, p. XI. I find that Duhem was neither a naïve nor a sophisticated neo-Thomist. As Robert Deltete recently remarked, Duhem “tried to distance himself from” Thomists, and discouraged “fellows Catholics from using the results of science to promote Christian apologetics”. He undertook a two-fold task: “to cut off *both* any science-based attacks on religion *and* all possibility of a science-based natural theology”. (Deltete R. 2011, pp. 19-21)

<sup>39</sup> See Kragh H. 2008, pp. 113-7. I find quite convincing Kragh’s brief reconstruction of Duhem’s attitude. See, in particular, pp. 116-7: “According to Duhem, the controversy between Catholic thought and modern science was essentially a misunderstanding based in a failure to appreciate the separate domains of the two fields.” Kragh also noticed that Duhem conceptions “made him a target from some Catholics, who suspected him of philosophical scepticism”. (*Ibidem*, p. 117)



## *1. A Historical Framework for the Emergence of Thermodynamics*

In the last decades of the nineteenth century, the second Principle of Thermodynamics had become a very sensitive issue in physics. Not only had it triggered off a wide debate inside the community of physicists, but also between physicists and other scientists, and between physicists and philosophers. At the beginning of the last decade of the century, George H. Bryan and J. Larmor had been commissioned by the *British Association for the Advancement of Science* to clarify the foundations of the second Principle. The corresponding Report was drawn up by Bryan, and published by the Association in 1891. It appears as something less than a historical and critical analysis: it consists of a list of problems, and it is not conclusive in many respects. From the outset Bryan specified that his analysis dealt only with “the attempts that have been made to deduce the Second Law of Thermodynamics from purely mechanical principles”. Clausius’ “method” seemed to him the best, for it was “independent of any assumption regarding the nature of the intermolecular forces”.<sup>1</sup>

At the end of the century, W.F. Magie, Professor of Physics at Princeton University, edited some memoirs by Carnot, Clausius and W. Thomson, under the title *The Second Law of Thermodynamics*. At that time, Thermodynamics had already been acknowledged as one of the fundamental fields of physical sciences. It seemed that the first and second laws really mirrored fundamental features of the universe as a whole.<sup>2</sup>

Around the middle of the nineteenth century, three research programmes were at stake in the context of the sciences of heat: Fourier’s mathematical theory of heat propagation, Carnot’s phenomenological theory of thermal engines, and different theories and conjectures on the preservation and transformations of energy. Two main characters attempted to transform the mathematical and conceptual contents stemming from the three programmes into a consistent theory: Rudolf Clausius and William Thomson. Clausius’ pivotal concept was the “content of transformation” or “Verwandlungsinhalt”, which he labelled “Entropie” in 1865; W. Thomson’s concept of “dissipation” also encompassed the different thermal processes. The new terms and the corresponding concepts were accepted by scientists only after reinterpretations, misinterpretations and hesitations, and continued to be debated far beyond the turn of the twentieth century.<sup>3</sup>

In 1849, Thomson reminded the readers about Carnot’s theory of thermal engines. Carnot had assumed that, in an ideal thermal engine, “at the end of a cycle of operations”, when the physical system comes back “to its primitive physical condition”, the quantity of heat absorbed “during one part of the operations” is wholly given out “during the remainder of the cycle”. Nevertheless, heat could be generated by friction, and this fact did not match with the representation of heat as a preserved substance: therefore Thomson wondered if the theory of thermal engines might “ultimately require to be reconstructed upon another foundation”. However he stated that “a certain quantity of heat is *let down*” from the boiler to the

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<sup>1</sup> Bryan G.H. 1891, pp. 85 and 121.

<sup>2</sup> According to Magie, the “science of Thermodynamics” had “laid the foundation for the Science of Chemical Physics”, and had “furnished a general view of the operations of the universe” when associated to “the kinetic theory of gases, as developed by Maxwell and Boltzmann”. (Magie W.F. 1899, p. vi)

<sup>3</sup> Clausius’ papers on Thermodynamics are collected in *Abhandlungen über die Mechanische Wärmetheorie*, which appeared in two volumes, the first being published in 1864, and the second in 1867. Some of W. Thomson’s papers were later collected in the first volume of *Mathematical and Physical Papers*, which was published in 1882, and in *Popular Lectures and Addresses*, which was published in 1889.

condenser, more in general from a hot body ... to another body at a lower temperature”, and that the “thermal agency by which mechanical effect may be obtained, is the transference of heat from one body to another at a lower temperature”.<sup>4</sup>

The following year Clausius acknowledged that he had become acquainted with Carnot’s researches on the theory of steam machines through Clapeyron and W. Thomson’s re-interpretation. According to Clausius, the core of Carnot’s theory could be synthesised in two statements: the mechanical work performed by heat required that “a certain quantity of heat passes from a warm to a cold body”, and “no heat gets lost, but its quantity remains unchanged”, as Carnot himself had “explicitly” stated. With regard to the second statement, some objections could be raised: if we assume that the quantity of heat must be preserved like the quantity of a substance, then “we should also assume that such a quantity cannot increase”. Nevertheless, Joule had shown that heat could be generated by friction, and “other facts” supported the view that “heat is not a substance, but consists in a motion of the smallest parts of bodies”.<sup>5</sup>

Clausius concluded that a principle of equivalence between heat and mechanical work had to be assumed, and that work stemmed from “an actual *consumption* of heat” rather than from a mere rearrangement in the *distribution* of heat; conversely “heat could be *generated* by the consumption of work”. Carnot’s “fundamental principle could be preserved” by assuming that “a given amount of heat is consumed, another is transferred by a warm to a cold body, and there is a definite relation between the two quantities of heat and the performed work”. In the new theory, the basic assumption on “the equivalence between heat and work” could be associated to “Carnot’s basic assumption” that the performance of mechanical work required the transfer of heat from a boiler to a cooler.<sup>6</sup>

In 1851 Thomson credited Humphry Davy with having established the “dynamical theory of heat”, and Rankine and Clausius’ with having given “[i]mportant contributions”. Mayer and Joule were credited with having “demonstrated the immateriality of heat” and the “equivalence between mechanical work and heat”. He stated that he would have followed Rankine and Clausius’ track: they had put forward a “mathematical reasoning analogous to Carnot’s on the motive power of heat”, although “founded on an axiom contrary to his fundamental axiom” on “the permanence of heat”.<sup>7</sup>

Thomson avowed that he had “only recently become acquainted with Helmholtz’s admirable treatise on the principle of mechanical effect”, *Ueber die Erhaltung der Kraft*, wherein the author had put forward a specific principle of the conservation of energy (“Kraft”). Mayer and Joule’s researches on the convertibility between heat and mechanical work could be looked upon as a widening of the perspective on conservation. Thomson showed that the alliance between Carnot’s “proposition” or the “criterion of a perfect thermodynamic engine”, and Joule’s “principle” of convertibility led to a fundamental “axiom”. He acknowledged that Clausius had been the first to have established Carnot’s proposition “upon correct principles” the year before, even though Clausius’ statement had been expressed in a

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<sup>4</sup> Thomson W. 1849, in Thomson W. 1882, pp. 115 and 117-8. W. Thomson had held the chair of Natural Philosophy at Glasgow University since 1846.

<sup>5</sup> Clausius R. 1850, in Clausius R. 1864, pp. 17-8.

<sup>6</sup> Clausius R. 1850, in Clausius R. 1864, pp. 18, 20, and 48. In September 1850 Clausius became professor at the Royal Artillery and Engineering School in Berlin. See Gillispie C.C. (ed.), vol. III, p. 303.

<sup>7</sup> Thomson W. 1851, in Thomson W. 1882, pp. 174-7 and 185.

different form, and was then unknown to Thomson himself.<sup>8</sup> Thomson's axiom was expressed as follows:

*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*<sup>9</sup>

In a short paper W. Thomson published in the *Philosophical Magazine* in 1852, he started from "Carnot's proposition that there is an absolute waste of mechanical energy available to man", when "heat is allowed to pass from one body to another at a lower temperature". Thomson specified that what he had labelled "Carnot's proposition" made reference to very general devices which did not necessarily satisfy the requirement of being a "perfect thermodynamic engine". Moreover, in Thomson's words, Carnot's theory had already become a re-interpretation of Carnot's original theory: it was a new theory based "on a new foundation", namely "the dynamical theory of heat". He then specified that the waste of energy "cannot be annihilation, but must be some transformation of energy".<sup>10</sup>

In the following passages he listed different sources of the "*dissipation* of mechanical energy": the transformation of mechanical work into heat in reversed thermal engines was placed next to friction, thermal conduction, and thermal radiation.

When heat is created by a reversible process (so that the mechanical energy thus spent may be *restored* to its primitive condition), there is also a transference from a cold body to a hot body of a quantity of heat bearing to the quantity created a definite proportion depending on the temperature of the two bodies.

When heat is created by any unreversible process (such as friction), there is a *dissipation* of mechanical energy, and a full *restoration* of it to its primitive condition is impossible.

When heat is diffused by *conduction*, there is a *dissipation* of mechanical energy, and perfect *restoration* is impossible.

When radiant heat or light is absorbed, otherwise than in vegetation, or in chemical action, there is a *dissipation* of mechanical energy, and perfect *restoration* is impossible.<sup>11</sup>

Thomson's pivotal concept was "*dissipation*": it dealt with the distinction between "reversible" and "unreversible", and with the possibility or impossibility of a perfect "*restoration*". In the end, he drew some general conclusions:

1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.
2. Any *restoration* of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, ...

<sup>8</sup> Thomson W. 1851, in Thomson W. 1882, pp. 180-3, the footnote at pp. 182-3 included.

<sup>9</sup> Thomson W. 1851, in Thomson W. 1882, p. 179.

<sup>10</sup> Thomson W. 1852, in Thomson W. 1882, p. 511.

<sup>11</sup> Thomson W. 1852, in Thomson W. 1882, p. 512. Thomson did not disentangle the Carnot from the Fourier processes. See Brush S.G. 2003a, p. 484.

3. Within a finite period of time past, the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject.<sup>12</sup>

In 1854, once again Clausius 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.

*In allen Fällen, wo eine Wärmemenge in Arbeit verwandelt wird, und der diese Verwandlung vermittelnde Körper sich schliesslich wieder in seinem Anfangszustande befindet, muss zugleich eine andere Wärmemenge aus einem wärmeren in einem kälteren Körper übergehen, und die Grösse der letzteren Wärmemenge im Verhältnis zur ersteren ist nur von den Temperaturen der beiden Körper, zwischen welchen sie übergeht, und nicht von der Art des vermittelnden Körpers abhängig.<sup>13</sup>*

His 1854 paper consists of a short Introduction, and two sections. The first was devoted to the first Principle, and its title was “Satz von der Aequivalenz von Wärme und Arbeit”; the second, whose title was “Satz von der Aequivalenz der Verwandlungen”, dealt with the second Principle. The linguistic symmetry between the two Principles is worth remarking, as well as the fact that he gave two formulations of the second principle.<sup>14</sup> In the second formulation, the second law became a law of equivalence between “transformations”, in order to maintain a sort of symmetry in the axiomatic structure of Thermodynamics. This formulation of the second law, pivoted on the concept of “equivalence value”  $Q/T$ , where  $T$  was a function of temperature. From the linguistic and conceptual points of view, the two laws of Thermodynamics were nothing else but two principles of equivalence: if the first stated the equivalence between heat and work, the second stated the equivalence between mathematically well-defined values of “transformation”.

<sup>12</sup> Thomson W. 1852, in Thomson W. 1882, p. 514.

<sup>13</sup> Clausius R. 1854, in Clausius R. 1864, p. 133. See also pp. 127-8.

<sup>14</sup> In the first formulation we read: “... es kann nie Wärme aus einem kälteren in einen wärmeren Körper übergehen, wenn nicht gleichzeitig eine andere damit zusammenhängende Aenderung eintritt” (Clausius R. 1854, in Clausius R. 1864, p. 134). In a long footnote, which Clausius added ten years later, when the present paper was re-published in his *Abhandlungen über die mechanische Wärmelehre*, he put forward other expressions for the above statement: “die Wärme kann nicht von selbst aus einem kälteren in einen wärmeren Körper übergehen”, and “ein Wärmeübergang aus einem kälteren in einen wärmeren Körper kann nie ohne Compensation stattfinden”. He remarked that the word “Compensation” had the same meaning of the expressions “von selbst” and “wenn nicht gleichzeitig eine andere damit zusammenhängende Aenderung eintritt”. (*Ibidem*, pp. 134-5, footnote 1)



Nennt man zwei Verwandlungen, welche sich, ohne dazu eine sonstige bleibende Veränderung zu erfordern, gegenseitig ersetzen können, äquivalent, so hat die Entstehung der Wärmemenge  $Q$  von der Temperatur  $t$  aus Arbeit den Aequivalenzwerth

$$\frac{Q}{T},$$

und der Uebergang der Wärmemenge  $Q$  von der Temperatur  $t_1$  zur Temperatur  $t_2$  den Aequivalenzwerth

$$Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

worin  $T$  eine von der Art des Processes, durch welchen die Verwandlung geschieht, unabhängige Temperaturfunction ist.<sup>15</sup>

He assumed the transformation of work into heat as a positive quantity, and the transfer of heat from a high to a low temperature equally positive. In the case of  $K_1, K_2, \dots, K_n$  bodies, to be found at the temperatures  $t_1, t_2, \dots, t_n$ , he assumed that the quantities  $Q_1, Q_2, \dots, Q_n$  of exchanged heat were positive when received, and negative when sent off. Then he defined a quantity  $N$  as the sum of all “the values of transformation”

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

In general, when temperatures changed in the course of every 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 ( $\oint dQ/T = 0$ ), as required by a law of conservation: the sum of all contribution along a closed path must necessarily vanish.<sup>16</sup>

A formal analogy between Mechanics and Thermodynamics was thus established. The sum of “the contents of transformation (Verwandlungsinhalt)” had to vanish in pure, “reversible (umkehrbar)” thermodynamic processes, as well as the sum of mechanical works along a closed path had to vanish in pure mechanics, wherein dissipative effects were neglected. When the processes were irreversible, there was a loss of “Verwandlungsinhalt”, and the above integral became positive: the initial conditions could not be restored, and the transformation was “uncompensated”.

Wir werden uns nun zur Betrachtung der nicht *umkehrbaren Kreisprocesse*.

<sup>15</sup> Clausius R. 1854, in Clausius R. 1864, p. 143.

<sup>16</sup> Clausius R. 1854, in Clausius R. 1864, pp. 140, 144-5, and 147.

Es wurde bei dem Beweise des Satzes, dass in einem beliebig zusammengesetzten umkehrbaren Kreisprocesse die algebraische Summe aller Verwandlungen Null sein müsse, zuerst gezeigt, dass die Summe nicht *negativ* sein könne, und dann wurde hinzugefügt, sie könne auch nicht *positiv* sein, weil man sonst den Process nur umgekehrt auszuführen brauchte, um eine negativ Summe zu erhalten. Der erste Theil dieses Beweises bleibt nun ungeändert auch für die nicht umkehrbaren Kreisprocesse gültig, der zweite dagegen kann bei diesen keine Anwendung finden. Man erhält also folgenden Satz, welcher für alle Kreisprocesse gemeinsam gilt, indem die umkehrbaren darin den Gränzfall bilden.

*Die algebraische summe aller in einem Kreisprocesse vorkommenden Verwandlungen kann nur positiv sein.*

Wir wollen eine solche Verwandlung, welche am Schlusse eines Kreisprocesses ohne eine andere entgegengesetzte übrig bleibt, und welche nach diesem Satze nur positiv vorkommen kann, kurz eine *uncompensirte* Verwandlung nennen.<sup>17</sup>

Among the processes which brought about “uncompensated transformations” Clausius mentioned “the transfer of heat by conduction”, which took place “between two bodies at different temperatures, placed in close contact”. Other cases were “the production of heat by friction”, and “the production of heat by an electric current” which flowed against “the electric resistance of the conductor”. In general, these processes dealt with forces that had to overcome some kinds of “resistance”, which were not “equal” to the external forces: the production of macroscopic “motions of considerable velocity” was therefore allowed. A fraction of the corresponding *living force* was “later transformed into heat”. Clausius remarked that the irreversible sudden expansion of a gas into a contiguous empty volume was a phenomenon of the same kind. When the gas, contained in a certain vessel, diffused freely into the contiguous empty vessel, the velocity of some parts increased, and their living force increased accordingly. Short afterwards “it came to rest once again”, when the process of diffusion was accomplished. In “the whole mass of gas” as much heat was available as it was before the expansion, and therefore “no heat was transformed into mechanical work”. On the other hand, an irreversible transformation had taken place: the gas could not be “compressed into the previous volume”, unless “some mechanical work was transformed into heat”.<sup>18</sup>

In 1857 Clausius put forward an abstract model of gas contained in a closed vessel, a mechanical model indeed. It was based on three assumptions, which involved three “vanishingly small” physical entities: the volume of molecules and the duration and intensity of molecular interactions.

Damit das Mariotte'sche und Gay-Lussac'sche Gesetz und die mit ihm in Verbindung stehenden Gesetze streng gültig seyen, muss das Gas in Bezug auf seinen Molecularzustand folgenden Bedingungen genügen.

- 1) Der Raum, welchen die Molecüle des Gases wirklich ausfüllen, muss gegen den ganzen Raum, welchen das Gas einnimmt, verschwindend klein seyn.
- 2) Die Zeit eines Stosses, d.h. die Zeit, welche eine Molecül, indem es gegen ein anders Molecül oder eine feste Wand stösst, bedarf, um seine Bewegung in der Weise zu ändern, wie es durch den Stoss geschieht, muss gegen die Zeit, welche zwischen zwei Stößen vergeht, verschwindend klein seyn.

<sup>17</sup> Clausius R. 1854, in Clausius R. 1864, pp. 151-2.

<sup>18</sup> Clausius R. 1854, in Clausius R. 1864, p. 152.

3) Der Einfluss der Molecularkräfte muss verschwindend klein seyn.<sup>19</sup>

The smallness of the interaction between couples of molecules or between a gas molecule and a vessel molecule allowed Clausius to set up a simplified physical model, where a sharp asymmetry was at stake. Microscopic molecular motions underwent two kinds of separate, complementary processes: continuous predictable trajectories, and sudden discrete collisions.

Zunächst wird gefordert, dass die Kraft, mit welcher die sämtlichen Molecüle sich in ihren mittleren Entfernungen noch gegenseitig anziehen, gegen die aus der Bewegung entstehende Expansivkraft verschwindet. Nun befinden sich aber die Molecüle nicht immer in ihren mittleren Entfernungen von einander, sondern bei der Bewegung kommt oft ein Molecül in unmittelbare Nähe eines anderen oder einer ebenfalls aus wirksamen Molecülen bestehenden festen Wand, und in solchen Momenten treten natürlich die Molecularkräfte in Thätigkeit. Die zweite Forderung besteht daher darin, dass die Theile des von einem Molecüle beschriebenen Weges, auf welchen diese Kräfte von Einfluss sind, indem sie die Bewegung des Moleculs in Richtung oder Geschwindigkeit merklich ändern, gegen die Theile des Weges, auf welchen die Kräfte als unwirksam betrachtet werden können, verschwinden.<sup>20</sup>

The new science of Thermodynamics split into two different but intertwined pathways: general concepts and laws, on the one hand, and microscopic mechanical models, on the other. Clausius was interested in undertaking both of them. In 1862 Thomson returned to the concept of “dissipation” and “irreversible action in nature”.

The second great law of Thermodynamics involves a certain principle of irreversible action in nature. It is just shown that, although mechanical energy is indestructible, there is a universal tendency to its dissipation, which produces gradual augmentation and diffusion of heat, cessation of motion, and exhaustion of potential energy through the material universe.<sup>21</sup>

The dissipation would have led the universe to “rest and death, if the universe were finite and left to obey existing laws”. The two hypotheses were far from being fulfilled, because Thomson was not inclined “to conceive a limit to the extent of matter in the universe”, and to look upon the whole universe as “a single finite mechanism, running down like a clock, and stopping for ever”. Moreover, he could not exclude “an overruling creative power”, in order to explain “either the beginning or the continuance of life”. As a result, he was reluctant to accept the “death” of the universe, and he restrained himself from drawing any “conclusions of dynamical science regarding the future condition of the earth”. He did not believe that Thermodynamics could utter the last word on the destiny of the universe. He would have

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<sup>19</sup> Clausius R. 1857, in Clausius R. 1867, p. 235. On the re-emergence of old kinetic theories of heat in Clausius’ mechanical model, see Stengers I. 2003, p. 230: “Associée à Bacon, Boyle, Hooke, Leibniz, puis à Rumford and Davy, elle ne produisit pas de pratique de mise en mesure, contrairement à la théorie calorique, et les spécialistes du calorique purent en faire l’exemple type de spéculation stérile. Mais elle restait disponible, et lorsque la conservation de l’énergie tua le calorique, James Joule, von Helmholtz and d’autres l’invoquèrent immédiatement comme alternative prometteuse à la théorie de la chaleur-substance. Cependant, c’est Clausius, encore lui, qui, dans son article «Sur le genre de mouvement que nous appelons chaleur» (1857), a créé l’innovation ...”

<sup>20</sup> Clausius R. 1857, in Clausius R. 1867, pp. 235-6.

<sup>21</sup> Thomson W. 1862, in Thomson W. 1889, p. 349.

confined himself to discussing the “limits to the periods of time, past and future, during which the sun can be reckoned on as a source of heat and light”.<sup>22</sup>

The same year Clausius tried to deepen his 1854 approach, and in 1865 he put forward a theoretical synthesis which soon became well known. From the outset he reminded the reader that he had devoted his efforts to pursuing a better comprehension of the second Law, whose “comprehension was much more difficult than the first one”. He aimed to express the law “in the simplest and, at the same time, general form”, and to show “its necessity”. Differently from previous papers, he had computed “as positive the entering quantity of heat, and as negative that sent off”. As a consequence, the second law could be translated into the general relation

$$\oint \frac{dQ}{T} \leq 0,$$

where the equality made reference to “cycles taking place in a reversible way”, and the inequality to “irreversible transformations”.<sup>23</sup>

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,

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

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  $dH/T$ , which was “a complete differential”, had already been labelled “value of transformation” by Clausius both in 1854 and 1862. In 1862 the second term  $Z$  had been labelled “Disgregation”: it depended on the “arrangement of the parts of the body”, and its increase corresponded to “the transformation

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<sup>22</sup> Thomson W. 1862, in Thomson W. 1889, pp. 349-50. From a more general point of view, it sounds quite surprising that W. Thomson associated the thermodynamic consumption of the universe to the metaphor of the clock, when we consider that the clock had been the metaphor of a mechanical universe. On the other hand, mechanical metaphors are consistent with Thomson’s mechanical world-view. Moreover, he probably thought that even a mechanical universe required some kind of restoration, as Newton had surmised almost two century before. In the subsequent years, W. Thomson made use of thermodynamics to compute the finite age of the Sun: the computation allowed him to attack recent geological and biological theories, which required much more time to explain the natural evolution. See Thomson W. 1887, p. 390. For a synthetic account of the debate between physicists and geologists on the age of the Earth, and the role played specifically by the second law of thermodynamics, see Brush S.G. 1978, chapter III.

<sup>23</sup> Clausius R. 1865, in Clausius R. 1867, pp. 1 and 3.

of work into heat". When compared to Thomson's *dissipation*, which encompassed both Carnot-like and Fourier-like processes, Clausius' *Disgregation* appears as a more specific concept which made reference to molecular disorganisation.<sup>24</sup>

Clausius reported that he had been looking for a new word for the entity  $S$ , which would have emphasised the linguistic and conceptual analogies between the "content of transformation" and the energy  $U$ . He chose the word "Entropie" as a German transliteration of the Greek word "*εντροπη*", whose semantic field also 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 value of transformation and the disgregation. The formal analogy between the first and second laws of thermodynamics, which he had put forward in 1854, resulted further strengthened. 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". According to Clausius, six physical entities were at stake in "the mechanical theory of heat":

1. "the content of heat",
2. "the content of work",
3. their sum, namely "the energy",
4. "the value of transformation of the content of heat",
5. "the disgregation",
6. and their sum, namely "the entropy".<sup>25</sup>

Clausius' "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 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.<sup>26</sup>

Might this theoretical approach be looked upon as an attempt to follow Thomson's cosmological trend? In any case, both scientists and philosophers found it quite attractive: the word "entropy" entered scientific, philosophical and theological debates, whereas "Verwandlungsinhalt" and "Disgregation" faded into the background. Clausius' 1854

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<sup>24</sup> Clausius R. 1865, in Clausius R. 1867, pp. 31-3. In his 1862 paper "Über die Anwendung des Satzes von der Aequivalenz der Verwandlungen auf die innere Arbeit", the term  $dH$  had also been qualified as "the value of transformation of the quantity of heat computed in the initial state". (*Ibidem*, p. 33) The word "Disgregation" did not appear in the monumental dictionary of German language the Grimm brothers were developing in the same years.

<sup>25</sup> Clausius R. 1865, in Clausius R. 1867, pp. 34-5.

<sup>26</sup> Clausius R. 1865, in Clausius R. 1867, p. 44.

approach had managed to disentangle the different physical processes which Thomson had collected under the label “dissipation”, namely the Fourier and Carnot processes. Moreover, making use of the language and concepts of Analytical Mechanics, Clausius let 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 the “Verwandlungsinhalt” was conserved in ideal thermodynamic processes without dissipation. When expressed as a law of conservation, the second Principle also echoed a formal analogy with Carnot’s conservation of *caloric*. In Clausius’ theory, *caloric* did not undergo conservation any more; it was replaced by a more abstract and sophisticated physical entity, “Verwandlungsinhalt”, which underwent conservation in ideal thermal engines.

At the end of the nineteenth century, Duhem was able to understand and appreciate Clausius’s multifarious heritage. In 1893, when he compared the meta-theoretical attitudes of British scientists with Continental scientists’ attitudes, he focussed on the principles of Thermodynamic as put forward by W. Thomson and Clausius. If he found in Thomson some “paradoxical” aspects even in the interpretation and applications of “the widely accepted theories”, he credited Clausius with having managed to derive “the new laws” in a “natural” way from “the already known principles”.<sup>27</sup>

In 1895, in a series of three papers devoted to the “theories of heat”, he outlined a historical reconstruction of the transition from the caloric to the dynamic theory of heat. He did manage to grasp that, in spite of its well-known flaws, the caloric theory could be abandoned only after the emergence of a new reliable theory. In order to overcome and replace an old theory, something more complex than a simple hypothesis was required.

Laplace, Berthollet, Desormes et Clément, tous les partisans de la théorie du calorique savent que le frottement dégage de la chaleur ; tous, ils avouent plus ou moins nettement que ce fait constant, indéniable, contredit leurs hypothèses ; ils continuent cependant à raisonner comme si ces hypothèses étaient vraies ; la supposition que la chaleur est la manifestation sensible d’une certaine substance matérielle ne sera abandonnée que lorsqu’une théorie nouvelle , regardant la chaleur comme l’effet produit sur nos organes par un genre particulier de mouvement, aura rendu compte non seulement des phénomènes expliqués par les partisans du calorique, mais encore de ceux que leurs adversaires leur objectaient<sup>28</sup>

Moreover he found that, in the first half of the nineteenth century, the recently discovered analogies between light radiation and heat radiation had had a deep influence on the whole body of the science of heat. The transition from an emission theory to a dynamical or wave-theory of light, which had taken place in the first half of the century, had induced a correspondent conceptual shift in the theories of heat. In the context of emerging Thermodynamics, heat became a physical entity intrinsically *linked* to a *process*, rather than an entity intrinsically *contained* in a given *space*.<sup>29</sup>

<sup>27</sup> Duhem P. 1893e, pp. 138-9.

<sup>28</sup> Duhem P. 1895c, in Duhem P. 1992, p. 399.

<sup>29</sup> Duhem P. 1895c, in Duhem P. 1992, pp. 401 and 411.

Duhem focussed on Clausius' concept of "equivalent transformation", and on its conceptual link with Carnot's ideal thermal engine, wherein the sum of the terms  $dQ/T$  along the cycle vanished. In the case of "a system describing a real, non-reversible cycle", we are not sure that positive transformations balance exactly the negative ones. He specified that Clausius had "stated" that the two sets of transformation "never balance exactly", but he had not managed to "demonstrate" it. He had shown, in particular, that "the sum of all the transformations produced along a real cycle was always positive".<sup>30</sup>

Duhem sharply criticised the kinetic theory of gases: in general, he did not trust in specific mechanical models. He claimed that even Clausius had regarded the mechanical models of heat with suspicion. He attributed to Clausius the distinction and the mutual independence between "pure thermodynamics" and "kinetic theory". According to Duhem, it would be better to start from the relationship between heat and mechanical work in a cyclic transformation rather than from some assumptions on the nature of heat. The theoretical structure of thermodynamics did not depend on the specific mechanical models of microscopic motions, and that structure did not have to be put in danger whenever doubts were cast on those models. His abstract and formal approach to Thermodynamics led him to look upon "the amount of heat" as a simple "abstraction, whose precise meaning depends on the specific model assumed".<sup>31</sup>

In 1903, Duhem synthesised the theoretical and historical researches he had undertaken in the field of thermodynamics in the previous years. Those researches had led him to a great design of unification of physics, and to a critical review and a re-interpretation of the history of physics. In the book he published, *L'évolution de la Mécanique*, he tried to put Clausius' theory against the background of a long-lasting competition between different scientific traditions. In the course of the history of physics Duhem saw the emergence of different kinds of "mechanics": Descartes' mechanics, "atomistic mechanics", Newton's mechanics, Lagrange's "analytical mechanics", and Poisson's "physical mechanics". Duhem appreciated the independence of Carnot-Clausius' principle of any hypothesis on the nature of heat, and of any specific mechanical model.

À la découverte de ce dernier principe, les suppositions sur la nature mécanique de la chaleur n'ont nullement contribué ; des postulats, que l'induction avait tirés du sein des vérités d'expérience, ont conduit Sadi Carnot à l'énoncer sous une forme qui impliquait l'hypothèse du Calorique ; plus tard, Clausius l'a modifié de telle manière qu'il pût s'accorder avec le Principe de l'équivalence entre la chaleur et le travail ; les énoncés divers que ce grand physicien en a donné sont indépendants de tout ce qui a été tenté pour expliquer les propriétés de la chaleur par les lois de la force et du mouvement.<sup>32</sup>

According to Duhem, the most important achievement of Thermodynamics was the integration between the different conceptual streams which had contributed to the development of the science of heat in the first half of the nineteenth century. Two theoretical approaches, which corresponded to two classes of idealised phenomena were at stake: fluxes of heat without any mechanical effect in Fourier's theory, and the mechanical work performed by heat without any thermal dissipation in Carnot's theory. Until the emergence of

<sup>30</sup> Duhem P. 1895c, in Duhem P. 1992, pp. 419 and 422.

<sup>31</sup> Duhem P. 1895c, in Duhem P. 1992, pp. 436-9.

<sup>32</sup> Duhem P. 1903, in Duhem P. 1992, p. 110.

Thermodynamics, around the middle of the century, the two theories had not communicated with each other, although thermal propagation or dissipation strongly influenced and limited the actual production of mechanical work in thermal engines. The accomplishment of that necessary integration had been one of the most important aims of Duhem's theoretical researches in the previous years.<sup>33</sup>

The existence of irreversibility and dissipation in actual natural processes had shown how problematic the conceptual links between Mechanics and Thermodynamics really were. In particular, a mechanical explanation of dissipation clashed with the time reversibility of mechanical equations. Duhem remarked that "*all kinds of motion ruled by d'Alembert and Lagrange's Dynamics are reversible motions*". On the other hand, anyone could notice that "*natural motions are not reversible*". From the merely mathematical point of view, forces which depend on velocity could really give rise to the time irreversibility which we observe in the natural world, as Lagrange himself had pointed out. Nevertheless, from the physical point of view, that mathematical choice seemed not consistent with the invariance of physical processes with regard to uniform rectilinear motions: in Duhem's words, "the actual forces experienced by a mechanical system at rest in a given state do not change if that state takes place in the course of some motion".<sup>34</sup>

In the first half of the twentieth century, not only did Duhem's theoretical physics become a sort of buried memory, but even his history of modern physics faded away into oblivion. Only in the last decades of the twentieth century, some aspects of his historical reconstruction re-emerged and were further developed.

In 1976, Stephen Brush revived Duhem's historical reconstruction of the progressive abandonment of the caloric theory, in particular the role played by the wave-theory of light. He stressed the role of Clausius in that conceptual shift: it had been Clausius who, in 1857, had "defined the scope and viewpoint of most 19<sup>th</sup>-century work in the kinetic theory of gases".<sup>35</sup>

Both Clausius and W. Thomson were interested in the kinetic theory of gases, but Thomson upheld a more radical kind of atomism, "the vortex theory" of atoms. It was a "purely kinetic" theory, which eliminated "the need to postulate arbitrary intermolecular forces". Atoms were looked upon as permanent rotational structures which could freely emerge from a continuous medium like aether. Brush remarked that the caloric theory and the kinetic theory shared the same mechanistic hallmark: both of them reduced "complex phenomena to mere matter and motion". If the former explained heat "in terms of *matter*", the latter explained it "in terms of *motion*". Brush also remarked that physical theories put forward in the early nineteenth century "were apparently based on the caloric theory", even though "it was later found that

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<sup>33</sup> See Duhem P. 1903, in Duhem P. 1992, p. 268: "Cette théorie, imaginée comme l'on sait par Fourier, devient ainsi l'auxiliaire indispensable de la Thermodynamique; elle seule rend possible la formation des relations supplémentaires sans lesquelles la mise en équation du problème de la Dynamique serait incomplète."

<sup>34</sup> See Duhem P. 1903, in Duhem P. 1992, pp. 141-3.

<sup>35</sup> See Brush S.G. 1976, book 1, pp. 31-2, 160, and 168; book 2, pp. 306, 316, and 319. See also Brush S.G. 1978, pp. 9-10. Brush stressed the mathematical mismatch between wave-equations and equations of heat transport, in particular the difference between "second-order differential equations in time" for "the propagation of heat by waves", and "first-order time derivative" for "propagation as described by Fourier's heat conduction equation". See Brush S.G. 1976, book 2, p. 316. The physical law on heat radiation was put forward by the Austrian physicist Joseph Stefan in 1879, and then derived theoretically by Boltzmann in 1884. See Brush S.G. 1978, pp. 54-5.



they could be reformulated in a way that did not depend on the assumption of a conserved heat substance”.<sup>36</sup>

He stressed the role of W. Thomson in the complex process of integration between the Fourier and Carnot traditions: his universal law, which stated the “universal tendency towards dissipation of energy”, had merged “the theory of terrestrial refrigeration” with “the thermodynamic analysis of steam engines”.<sup>37</sup>

After a few years, the mathematical physicist and historian of physics Clifford A. Truesdell inquired into the relationship between the Fourier and Carnot traditions. He stressed two complementary contradictions: in Carnot’s theoretical approach, “thermal conduction is forbidden” in “perfect thermal engine”, and in Fourier’s theory of heat, Fourier had “regarded an increase of volume as the inevitable companion of an increase of temperature”, but his theory “sets aside the phenomenon by which, certainly, we are able to measure temperatures”. This would explain why “Fourier’s influence spanned from mathematics to physics, even though he did not influence thermodynamics”. Moreover, in his mathematical physics, “differences of temperature are diffused instantly through infinite distances”. Fourier and Carnot had developed two different, even mutually foreign, aspects of a general theory of heat. If Carnot had “set one great stone in the foundation of a general thermodynamics”, Fourier “had set another, at the opposite corner”. The fact is that “[c]ornerstones these were, not a framework or even a substructure”. Truesdell pointed out the underestimation of *time* in thermodynamic theories, although “time is the basic descriptor of natural changes”. Carnot had also got rid of “time”, and “all thermodynamicists were to follow Carnot”: from then onwards, “it came to seem impossible that thermodynamics could ever mention the time”.<sup>38</sup>

Truesdell’s appraisal of Clausius’ theoretical approach was swinging from warm appreciation to sharp criticism. At first he stated that “the tragicomic muse of thermodynamics casts her aura and her curse upon a man” who was “a penetrating student of nature but a feeble mathematician”. On the one hand, he credited Clausius with having “created classical thermodynamics”: he had “the quality of a great discoverer”, because he had managed to “*to unite previously disparate theories*”, in order to “construct a complete theory that is new yet firmly based upon previous partial successes”. In particular, he “*constructed the thermodynamics of ideal gases*”, and “*for those gases he discovered the internal energy*”. On the other hand, he claimed that “[f]ew mathematical physicists have shown so little sense of the right mathematics for the job”. With regard to the fundamental paper Clausius published in 1854, Truesdell confessed that his “verbal statement” of the “Second Law” made “no sense”, because it consisted merely of “a Mosaic prohibition”.<sup>39</sup>

<sup>36</sup> Brush stressed that “Maxwell was interested in the vortex theory for much the same reasons”. See Brush S.G. 1976, book 1, pp. 206-7. Among the early nineteenth-century theories he mentioned “Lavoisier’s theory of chemical elements” and “Laplace’s theory of the velocity of sound”, apart from “Fourier’s theory of heat conductions” and “Sadi Carnot’s theory of steam engines”. See Brush S.G. 1978, pp. 9 and 12.

<sup>37</sup> Brush S.G. 2003a, in Brush S.G. (Hall N.S. ed.) 2003, p. 484.

<sup>38</sup> Truesdell A.C. 1980, pp. 70, 72 (and fn. 7), 78, 90 and 135-7. See also Truesdell A.C. 1980, p. 143: “Between the “mechanical theory of heat” and the “analytical theory of heat”, created separately at about the same time, had been erected an adiabatic wall. One was a mathematical field theory, clearly stated, conceptually meagre, and abounding in initial-value problems and boundary-value problems. The other was a physical theory of lumped parameters, given to extravagant and altogether unjustified claims of generality, pregnant but abortive.”

<sup>39</sup> Truesdell A.C. 1980, pp. 185, 204, 206, and 215. Even for Clausius’ 1854 paper Truesdell’s criticism focussed on the mathematical side of the theory: if “philosophers and journalists have acclaimed this commandment”, mathematicians “have shuddered and averted their eyes from the unclean”. He found that “the oracles of CLAUDIUS” had frequently been “repeated, embroidered, and glossed in all the textbooks”, even though their

Although in a sharper and unpleasant way, Truesdell essentially shared Duhem's remark that Clausius had "stated" rather than "demonstrated" the validity of the second Law. The difference in style between Duhem and Truesdell's appraisals cannot mislead us: in reality they shared the same attitude towards Thermodynamics. Only three years before, in the Dedication of a previous book, Truesdell had expressed his "respectful gratitude for the legacy of the great French thermodynamicists CARNOT, REECH, DUHEM".<sup>40</sup>

In the present century, the historian of physics Jos Uffink underestimated Duhem's contribution to Thermodynamics: as a consequence, he looked upon the lack of *equations of motions* as an intrinsic feature of Thermodynamics.<sup>41</sup>

When in 1852 W. Thomson made reference to "a universal tendency in nature to the dissipation of mechanical energy", he gave the second Principle of Thermodynamics "a cosmic validity and eschatological implications". The processes which W. Thomson made reference to in 1852 were not cyclical processes in general, but "processes in which the final state is different from the initial state". According to Uffink, Clausius made reference to such transformation only ten years later, when he introduced "two abstruse quantities", namely the "*vorhandene Wärme*"  $H$  and the "*Disgregation*"  $Z$ , whose definition was "not very clear". Moreover "Clausius' definition differed considerably from Kelvin's 1852 notion of reversibility", for Clausius qualified a process as reversible "when it proceeds very gently" or it is "quasi-static": whether the initial state "is recoverable is another matter". Uffink found that something like the arrow of time was not at stake in the emergence of Thermodynamics around the middle of the nineteenth century. Only the other branch of the science of heat, namely Fourier's theory, could exhibit equations which depended explicitly on time, and solutions which were not invariant under the time-reversal transformation  $t \rightarrow -t$ .<sup>42</sup>

In the same years, but from a different historiographic perspective, Isabelle Stengers noted that "the intelligibility and soundness of Carnot's cycle" were based upon "the caloric theory, and that "its re-interpretation was quite a demanding task" when it was undertaken "in the new context of mutual conversion between mechanical work and heat". In Carnot's theory, the efficiency of the thermal engine stemmed from a general law that prevented mechanical work from emerging from nothing. For W. Thomson and Clausius' theories, the upper limit to the efficiency of a thermal engine, and the upper limit to the conversion of heat into mechanical work became harder to explain. The new law of conservation, namely the conversion of heat into mechanical work, required a new principle in order to account for the maximum efficiency. In the context of the principle of conservation of energy, the upper limit to the efficiency was quite enigmatic. More specifically, that limit could not be deduced by

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meanings have remained quite mysterious. According to Truesdell, "CLAUSIUS' first paper, while entangled and slack, was in aim and result constructive", whereas from his second paper onwards, "through the murk and gloom emerges a growing aura of retreat and impending failure." See Truesdell A.C. 1980, pp. 333, 335, and 337.

<sup>40</sup> See Duhem P. 1895c, in Duhem P. 1992, p. 422, and Truesdell C.A. and Bharatha S. 1977, *Dedication*.

<sup>41</sup> He stressed two specific hallmarks of Thermodynamics, which have differentiated it from the other fields of physical sciences. At first, "thermodynamics does not possess equations of motions", and this is "[i]n contrast to mechanics". Secondly, the "reference to states of the environment of a system already lends a peculiar twist to classical thermodynamics": it is a feature that "we do not meet in other theories of physics". See Uffink J. 2001, pp. 315-16 and 330.

<sup>42</sup> Uffink J. 2001, pp. 329-32, 336, and 389. He made reference to Thomson W. 1852, p. 512, and Clausius R. 1862, p. 247-8 and 272-9. He also pointed out some linguistic and conceptual differences between W. Thomson's "(ir)reversible" and Clausius' "(nicht) umkehrbar" transformations, and the corresponding difference between time (ir)reversibility and system (ir)recoverability. See Uffink J. 2001, pp. 315-9.

the principle of conservation: conservation and limitation to the efficiency appeared as disconnected requirements.<sup>43</sup>

According to Stengers, the conceptual drift towards a cosmological interpretation of thermodynamics stemmed from the attempt to give a “realistic” and “symmetric” character to the two Principles. If Thomson relied on the two “universal” principles of “conservation” and “degradation” of energy, Clausius referred the conservation of energy and the increase of entropy to the whole universe. If Thomson had founded the mythology of “the thermal death of the universe”, Clausius had found in the Universe “the only physical system which was intrinsically prevented from exchanging anything with an environment”. The law of the increase of entropy could rigorously be applied only to the universe itself.<sup>44</sup>

In 2008, the historian of science Helge Kragh inquired into the history of philosophical and theological debates on entropy. From the outset, he remarked that the concept of “irreversible and dissipative processes in nature appeared in natural philosophy many years before the second law of thermodynamics”: in particular, it had emerged from the sciences which we now label “geology and geophysics”. If the second law of Thermodynamics had been underestimated by some scientists, it had opened new perspectives for philosophers and theologians.<sup>45</sup>

As Kragh repeatedly pointed out, the second Principle was subject to different interpretations. W. Thomson had “never used the concept of entropy and only rarely referred to it”; he rather “preferred to speak of dissipation of heat or energy”. The fact is that the variation of entropy and the dissipation of heat do not overlap exactly, as Clausius had tried to show in 1862 and 1865, and Maxwell pointed out subsequently. Kragh also remarked that Duhem had “argued that the entropy law merely says that the entropy of the world increases endlessly”; he had not stated “that it has any lower or upper limit”. This is a very important issue: Duhem did “not agree with the understanding of entropy as a measure of molecular disorder”, whereas in Boltzmann’s statistical approach, “a time must come when the disorder of a system is at its maximum”, and therefore entropy “cannot increase endlessly”.<sup>46</sup>

In conclusion, it seems to me that, apart from Duhem, historians have essentially skipped Clausius’ attempt to put forward a formal analogy between the theoretical structures of Thermodynamics and Mechanics. They have mainly focussed on a very specific side of the

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<sup>43</sup> Stengers I. 2003, pp. 193-4. See, in particular, Stengers I. 2003, I, p. 194: “Or, la démonstration de Carnot était fondée sur un argument par l’absurde traditionnel en mécanique. Si un cycle hypothétique devait avoir un rendement supérieur, son couplage avec un cycle idéal de Carnot fonctionnant à l’envers, comme pompe à chaleur, produirait *gratuitement* du travail mécanique. Mais si la chaleur se convertit en travail, il n’y a plus d’absurdité puisque, en tout état de cause, le travail n’est pas produit gratuitement. Pourquoi, encore une fois, la chaleur ne pourrait-elle pas alors se convertir intégralement en travail? Le rendement optimal défini par le cycle idéal de Carnot est devenu énigmatique.”

<sup>44</sup> Stengers I. 2003, pp. 199-200.

<sup>45</sup> In 1852, in a short paper, Rankine had put forward an ingenious mechanism in order to allow the universe to escape dissipation; in 1863, in a quite longer paper, Clausius excluded that Rankine’s mechanism could really operate. The director of the Royal Institution John Tyndall had never mentioned entropy in the subsequent editions (from 1863 to his death in 1893) of his successful book *Heat Considered as a Mode of Motion*. On the other hand, philosophers like Herbert Spencer got involved in the scientific debates on the second Principle, and on its cosmological implications. See Kragh H. 2008, pp. 20, 41, 62, 105, and 217-8. Kragh made reference to Spencer’s book “*First Principles*, a work that appeared in 1862, and was subsequently published in many editions and impressions” (*Ibidem*, p. 105). Rankine’s paper “On the Reconcentration of the Mechanical Energy of the Universe” can be found in Rankine M. 1881, pp. 200-202; Clausius’ paper “Ueber die Concentration von Wärme- und Licht-strahlen und die Grenzen ihrer Wirkung” can be found in Clausius R. 1864, pp. 322-61.

<sup>46</sup> Kragh H. 2008, pp. 31 and 114-5. Maxwell’s specification can be found in Maxwell J.C. 1885, pp. 192-3.

relationship between Thermodynamics and Mechanics, where microscopic mechanical models and specific interpretations of irreversibility were at stake. In reality, in the second half of the nineteenth century, more abstract issues were also at stake: Gibbs and Helmholtz developed them, and paved the way to Duhem's subsequent researches. Those formal analogies, which Clausius had let emerge in a stage of his scientific enterprise, were transformed by Duhem into a wide and consistent programme of research.

## 2. Some Developments along the Second Pathway

In the second half of the nineteenth century, an interesting pathway to Thermodynamics was undertaken by engineers who were familiar with abstract generalisations and Analytical Mechanics. The most important difference between this pathway and Maxwell and Boltzmann's pathway dealt with the relationship between Thermodynamics and Mechanics. According to the former, a general mathematical framework had to be set up, without any reference to microscopic structure underlying the physical system under consideration. According to the latter, microscopic mechanical models, mixed with extra-mechanical hypothesis of probabilistic nature, were expected to account for the thermodynamic behaviour of macroscopic systems. Expressions like "mechanical theory of heat" had different meanings when interpreted in the two different perspectives: formal similarities between the mathematical structures of Thermodynamics and Mechanics in the first case, and specific mechanical models in the second.

In 1869, a French engineer took the path of a mathematical generalisation of Thermodynamics. In two short papers published in the *Comptes Rendus*, François Massieu tried to dress Thermodynamics with the garments of a general mathematical 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  $p dv$  was "thermally equivalent" to  $A p dv$ , wherein  $A$  was the well-known conversion factor between mechanical and thermal measures. The first principle could therefore be expressed by the equation

$$dQ = dU + A p dv.$$

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 complete differential  $dS$  of a function  $S$  of the variables which are sufficient to define the state of the body".<sup>1</sup>

After having chosen  $v$  and  $t$  (volume and temperature) as independent variables, and after some pages of derivations and other computations, he arrived at a function  $\psi$  whose differential

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<sup>1</sup> Massieu F. 1869a, p. 858.

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

was a complete differential of the same variables. Massieu labelled “*characteristic function of the body*” the function  $\psi$ . The most important mathematical and physical step consisted in deriving “all body properties dealing with thermodynamics” from  $\psi$  and its derivatives. Not only could  $U$  and  $S$  be expressed in terms of the function  $\psi$ , but also  $\psi$  could be expressed in terms of  $U$  and  $S$ :

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

Then Massieu introduced a second *characteristic function*  $\psi'$  in terms of the two variables  $t$  and  $p$ . He first defined a new function  $U' = U + A p v$ , 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,

$$\frac{U'}{T} = \frac{U}{T} + \frac{A p v}{T} = \frac{U}{T} + \text{const},$$

and  $\psi$  and  $\psi'$  resulted the same function, apart from a constant value.<sup>3</sup>

Massieu claimed that not only could  $U$ ,  $p$ ,  $v$ ,  $Q$  and  $S$  be derived from  $\psi$  and  $\psi'$ , but also the specific heats at constant pressure or volume  $k$  and  $k'$ , and the coefficient of dilatation at constant pressure or volume  $\beta$  and  $\beta'$  could as well. Conversely he was able to give the specific mathematical expressions of  $\psi$  and  $\psi'$  in terms of  $T$ ,  $v$ ,  $p$ , and the specific heats  $k$  and  $k'$ , for ideal gases, saturated vapours and superheated vapours.<sup>4</sup>

After seven years, in an essay of almost one hundred pages published in the *Mémoires 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

<sup>2</sup> Massieu F. 1869a, p. 859, and Massieu F. 1869b, p. 1058. In the first paper, Massieu did not distinguish partial from total derivatives.

<sup>3</sup> Massieu F. 1869b, pp. 1059-60.

<sup>4</sup> Massieu F. 1869b, pp. 1060-1.

unifying power of Thermodynamics, which he identified with “the mechanical theory of heat”.<sup>5</sup>

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.

Les principes fondamentaux de la thermodynamique peuvent être représentés par deux équations générales applicables à toutes les substances ; qu’on imagine, en outre, les formules ou équations spéciales qui expriment les diverses propriétés calorifiques et mécaniques d’un corps déterminé, telle que l’expérience peut les fournir directement, ces équations devront être compatibles avec les équations générales de la thermodynamique, dont on pourra alors faire usage pour réduire, par élimination, les formules relatives à chaque corps à un nombre moindre de relations. Je suis parvenu à effectuer cette élimination d’une façon entièrement générale, et je montre, dans ce mémoire, que toutes les propriétés d’un corps peuvent se déduire d’une fonction unique, que j’appelle *la fonction caractéristique de ce corps*, et dont je donne l’expression pour les divers fluides.<sup>6</sup>

He expected that new “data which we do not have yet” would have led to a successful application of his theoretical procedure. The engineer Massieu appreciated a theoretical practice which went “beyond observation”, and showed that “different properties of different bodies are connected to each other”. The mathematical basis of his theoretical thermodynamics consisted in the choice of two variables among  $v$ ,  $t$ , and  $p$ : the third variable, and the other functions  $U$ ,  $Q$  and  $S$  could be derived as functions of them. The two state functions  $U$  and  $S$ , which corresponded to two complete differentials, were not mutually independent: they could be derived from a sole function, namely his “characteristic function”.<sup>7</sup>

In this 1876 essay, the deduction of the characteristic function is shorter and simpler than in the previous paper. From  $dS = dQ/dT$  and  $dQ = dU + A p dv$ , we obtain  $T dS = dU + A p dv$ . The addition of the term  $S dt = S dT$  to both members yielded

$$T dS + S dT = dU + A p dv + S dT, \quad d(ST) = dU + A p dv + S dT,$$

$$d(ST - U) = A p dv + S dT.$$

Since the first member was a total differential, so was the second, and Massieu could write

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<sup>5</sup> See Massieu F. 1876, p. 2: “En ce qui concerne les propriétés mécaniques et calorifiques des corps, la thermodynamique, ou théorie mécanique de la chaleur, a comblé la lacune. En effet, des deux principes généraux qui servent de base à cette science nouvelle découlent des relations qui n’avaient pu trouver antérieurement une expression nette et vraiment scientifique.”

<sup>6</sup> Massieu F. 1876, pp. 2-3.

<sup>7</sup> Massieu F. 1876, pp. 3-8.

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

where the function  $H$  corresponded to the function  $\psi$  of the previous paper. Moreover

$$S = \frac{dH}{dt}, \quad A p = \frac{dH}{dv}, \quad U = ST - H \quad \text{or} \quad U = T \frac{dH}{dt} - H.^8$$

An important feature of ideal gases could be derived from the mathematical properties of the characteristic function, because their internal energy did not depend on volume but only on temperature. Expressions for  $k$ ,  $k'$ ,  $\beta$ ,  $\beta'$ , and the coefficient of compressibility were given in terms of  $H$  and its derivatives; conversely, explicit expressions for the characteristic function in terms of the independent variables  $t$  and  $v$  were given for ideal gases and saturated vapours.<sup>9</sup>

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  $\psi'$  of the previous paper. A two-fold strategy, both mathematical and physical, was at stake. On 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  $H'$ .

Ces formules pourront être d'un usage commode lorsque l'on connaîtra un corps par l'expression de sa chaleur spécifique  $k$  à pression constante, et par la loi qui lie son volume  $v$  à sa pression  $p$  et à sa température  $t$ ; elles permettront d'obtenir les expressions de  $S$  et de  $U'$ , et par suite l'expression de la fonction caractéristique  $H'$  de ce corps.<sup>10</sup>

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".

Lors donc qu'on voudra vérifier l'exactitude d'une loi, on l'exprimera au moyen de la fonction caractéristique; s'il s'agit d'une loi générale applicable à tous les corps, son expression devra se réduire à une identité; s'il s'agit d'une loi applicable seulement à une catégorie de corps caractérisés par certaines propriétés, l'expression de la loi devra encore se réduire à une identité lorsqu'on aura tenu compte de ces propriétés.<sup>11</sup>

The second part of Massieu's essay was devoted to the application of the "general theory" to ideal gases and overheated vapours. The theory of vapours was developed in great detail,

<sup>8</sup> Massieu F. 1876, pp. 9-10.

<sup>9</sup> Massieu F. 1876, pp. 10-25.

<sup>10</sup> Massieu F. 1876, p. 29.

<sup>11</sup> Massieu F. 1876, p. 43.



under different hypotheses on specific heats. In the end Mssieu hinted at the relationship between theory and experiments: he stressed both the unifying theoretical power of the characteristic function, and the importance of accurate experimental data for the determination of the function itself.<sup>12</sup>

In the meantime, in the 1850s, the Scottish engineer Macquorn Rankine had undertaken an original pathway to Thermodynamics. In 1855 he published a paper in the *Proceedings of the Philosophical Society of Glasgow*, where he put forward a unified account of mechanical and thermal effects. His fruitful integration between the tradition of the technical exploitation of heat, and the tradition of mathematical physics led to an original re-interpretation and unification of physics.<sup>13</sup> The headline of the paper, “*Outline of the Science of Energetics*” contained a new word, which made reference to both the universality of the concept of energy, and the design of generalisation of physics. In the seventh section of the paper, “*Nature of the Science of Energetics*”, Rankine tried to explain that design, and therefore the meaning of that word.

Energy, or the capacity to effect changes, is the common characteristic of the various states of matter to which the several branches of physics relate; if, then, there be general laws respecting energy, such laws must be applicable, mutatis mutandis, to every branch of physics, and must express a body of principles as to physical phenomena in general. [...]

The object of the present paper is to present, in a more systematic form, both these and some other principles, forming part of a science whose subjects are material bodies and physical phenomena in general, and which it is proposed to call the SCIENCE OF ENERGETICS.<sup>14</sup>

From the outset, explicit meta-theoretical commitments emerge from Rankine’s paper. He identified two subsequent steps in scientific practice: if the first step consisted in deriving “formal laws” from experimental data on “an entire class of phenomena”, the second consisted in deriving those laws from a consistent “system of principles”. It was the second step which allowed scientists to reduce a scattered set of physical laws to “the form of science”. Then 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

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<sup>12</sup> See Massieu F. 1876, p. 92: “Je crois que la considération de la fonction caractéristique pourra être d’un grand secours le jour où l’on aura des déterminations expérimentales nouvelles. Cette fonction constitue un lien à la fois net et radical entre les coefficients que l’on considère habituellement dans les recherches physiques, en sorte qu’une connaissance plus complète d’un de ces coefficients pourrait perfectionner l’expression de la fonction caractéristique, et, par suite, celle des autres coefficients qu’on en déduit.”

<sup>13</sup> Rankine had just been appointed to the chair of civil engineering in Glasgow, and he had been Fellow of the *Royal Society* since 1853.

<sup>14</sup> Rankine M. 1855, in Rankine M. 1881, pp. 213-4.

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.<sup>15</sup>

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. He did not distrust models and analogies in the strict sense, for he tried to extend the formal framework of mechanics to all physics. He distrusted too specific mechanical models, in particular their narrow scope. According to Rankine, the adjective "hypothetical" could be interpreted in a realistic or instrumental way: the wave theory of light was an instance of realistic representation, whilst the concept of "magnetic fluid" an instance of instrumental. The fact is that Rankine did not reject the "hypothetical method" at any stage of the building up of a physical theory. The method could be useful "as a preliminary step", before undertaking the decisive step towards an "abstractive theory".<sup>16</sup>

The tradition of mechanics had provided scientists with plenty of "*mechanical*" models or "hypotheses".

The fact that the theory of motions and motive forces is the only complete physical theory, has naturally led to the adoption of *mechanical hypotheses* in the theories of other branches of physics; that is to say, hypothetical definitions, in which classes of phenomena are defined conjecturally as being constituted by some kind of motion or motive force not obvious to the senses (called *molecular* motion or force), as when light and radiant heat are defined as consisting in molecular vibrations, thermometric heat in molecular vortices, and the rigidity of solids in molecular attractions and repulsions.

The hypothetical motions and forces are sometimes ascribed to *hypothetical bodies*, such as the luminiferous ether; sometimes to *hypothetical parts*, whereof tangible bodies are conjecturally defined to consist, such as atoms, atomic nuclei with elastic atmospheres, and the like.<sup>17</sup>

In reality, Rankine 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

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<sup>15</sup> Rankine M. 1855, in Rankine M. 1881, p. 210.

<sup>16</sup> Rankine M. 1855, in Rankine M. 1881, pp. 210 and 213. 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 (See the *Foreword* in the present preview). Rankine's choice of labelling "*objective*" and "*subjective*" the two interpretations of the "hypothetical method" appears quite misleading.

<sup>17</sup> Rankine M. 1855, in Rankine M. 1881, p. 211.

“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”.<sup>18</sup>

At the same time, the tradition of mechanics offered structural analogies 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.<sup>19</sup>

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*.

“*Work*” is the variation of an accident by an effort, and is a term comprehending all phenomena in which physical change takes place. *Quantity of work* is measured by the product of the variation of the passive accident by the magnitude of the effort, when this is constant; or by the integral of the effort, with respect to the passive accident, when the effort is variable.

Let  $x$  denote a passive accident;

$X$  an effort tending to vary it;

$W$  the work performed in increasing  $x$  from  $x_0$  to  $x_1$ : then

$$\left. \begin{aligned} W &= \int_{x_0}^{x_1} X dx, \quad \text{and} \\ W &= X(x_1 - x_0), \quad \text{if } X \text{ is const.} \end{aligned} \right\}$$

Work is represented geometrically by the area of a curve, whereof the abscissa represents the passive accident, and the ordinate, the effort.<sup>20</sup>

<sup>18</sup> See Rankine M. 1853a, in Rankine M. 1881, p. 310. In his 1851 paper, he reminded the reader about a specific atomic model he had already outlined the year before. See Rankine 1851, in Rankine M. 1881, p. 49: “In that paper the bounding surfaces of atoms were defined to be imaginary surfaces, situated between and enveloping the atomic nuclei, and symmetrically placed with respect to them, and having this property – that at these surfaces the attractive and repulsive actions of the atomic nuclei and atmospheres upon each particle of the atomic atmosphere balance each other.”

<sup>19</sup> Rankine M. 1855, in Rankine M. 1881, pp. 214-6.

<sup>20</sup> Rankine M. 1855, in Rankine M. 1881, pp. 216-7.

The generalisation of the concept of work entailed the generalisation of the concept of energy, which was the core of Rankine 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 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:

$$U = \int_{x_1}^{x_0} X dx = -W.$$

In general, work was the result of “the variation of any number of independent accident, each by the corresponding effect”:

$$W = X dx + Y dy + Z dz + \dots^{21}$$

Rankine was aware that his generalised potential energy was a problematic concept, and that a sharp split between actual and potential energy could not grasp the complexity of some phenomena. Sometimes, what had been labelled actual energy might “possess the characteristics of potential energy also”: it could be accompanied “by a tendency or effort to vary relative accidents”. According to Rankine, heat represented an instance of actual energy, because of its specific feature of flowing from hot to cold bodies. But heat, “in an elastic fluid, is accompanied by a tendency to expand”, namely “an effort to increase the volume of the receptacle” containing the elastic fluid.<sup>22</sup>

However problematic they may be, Rankine submitted the new concepts of energy and work to three “*Axioms*”. The first concerned the universality and convertibility of energy: “*any kind of energy may be made the means of performing any kind of work*”, or, more formally, “[*a*]ll kinds of Work and Energy are Homogeneous”. Although “efforts and passive accidents to which the branches of physics relate are varied and heterogeneous”, all works and energies, the results of the multiplication between every effort and the corresponding accident, were physical quantities of the same kind. It was just this homogeneity which allowed energy to be transformed from one form into another. Rankine looked upon transformation and transference as different aspects of the same property.

... to *transform energy*, means to employ energy depending on accidents of one kind in putting a substance into a state of energy depending on accidents of another kind; and to *transfer energy*, means to employ the energy of one substance in putting another substance in a

<sup>21</sup> Rankine M. 1855, in Rankine M. 1881, pp. 217 and 222.

<sup>22</sup> Rankine M. 1855, in Rankine 1881, p. 218. In 1867, in response to John Herschel’s criticism, Rankine devoted a short paper to the meaning of the expression “potential energy”. There he distinguished between “energy of activity and energy of configuration”. Potential energy meant the “power of performing work which is due to configuration, and not to activity”. More specifically, he mentioned the relational character of potential energy: it was the “power of doing work dependent on mutual configurations”. The term “actual energy” was to be subsequently replaced with “kinetic energy” by Thomson and Tait. See Rankine M. 1867, in Rankine 1881, pp. 229-31. The Aristotelian *flavour* of words like accident, actual and potential would deserve a further analysis: on Rankine’s knowledge of classic philosophy see Tait P. G. 1880, p. xxi.

state of energy, both of which are kinds of work, and may, according to the axiom, be performed by means of any kind of energy.<sup>23</sup>

The second axiom concerned conservation: the total energy of a substance “*can be varied by external efforts alone*”, and “*cannot be altered by the mutual actions of its parts*”. According to Rankine, “of the truth of this axiom there can be no doubt”, for it could rely both on “experimental evidence” and on an independent theoretical “argument”. The argument had a cosmological implication: “the law expressed by this axiom is essential to the stability of the universe, such as it exists”. Rankine saw a logical link between the first and the second axiom. The second would imply the first: “*all work consists in the transfer and transformation of energy alone*” because “otherwise the total amount of energy would be altered”.<sup>24</sup>

Rankine’s third axiom is not so easy to grasp, but it is definitely the most original, and allows us to better understand his Energetics. 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 re-interpretation to all physical sciences. 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 must first take a look at two papers he had read before the Philosophical Society of Glasgow in January 1853, and then return to his 1855 paper.<sup>25</sup>

We must remember that, according to Rankine’s view, heat was a sort of actual energy with the tendency to transform into work in virtue of its “expansive power”, which was a sort of potential energy. What he labelled “thermometric” or “latent” heat had to be distinguished from the fluxes of heat between the physical system and its environment. The core of the computation was the determining of “the portion of the mechanical power  $PdV$  which is the effect of heat”: in other words, the fraction of actual energy transformed into work.<sup>26</sup>

The balance of energy, and the computation of the fraction of actual energy transformed into macroscopic work, led to applications and abstract generalisations. With regard to abstract generalisations, he claimed that the above computation could be applied “not only to heat and expansive power, but to any two convertible forms of physical energy”, provided that one was actual and the other potential. Then he gave “the principles of the conversion of energy in abstract”, which realised the passage from Thermodynamics to Energetics.<sup>27</sup>

This generalisation was the core of the third axiom Rankine put forward in his 1855 paper, the axiom he labelled “GENERAL LAW OF THE TRANSFORMATION OF ENERGY”. Under the label “transformation” he encompassed both transformations from actual energy into work and exchanges of actual energy. They were the generalisation of two different kinds of

<sup>23</sup> Rankine M. 1855, in Rankine M. 1881, p. 218.

<sup>24</sup> Rankine traced back the cosmological implication of the theoretical argument to Newton’s *Principia*, in particular the “Scolium to the Laws of Motion”. See Rankine M. 1855, in Rankine M. 1881, p. 218.

<sup>25</sup> Beside the already mentioned paper “On the Mechanical Action of Heat”, I will take into account the shorter “On the General Law of the Transformation of Energy”.

<sup>26</sup> Rankine M. 1853a, in Rankine M. 1881, pp. 311-13, and Rankine M. 1853b, in Rankine M. 1881, p. 203. The identification of “free heat” with the living force had already been put forward by Helmholtz in his *Ueberhaltung der Kraft*, in 1847. The “latent heat”, or “chemical forces of attraction” played the role of “tension forces”. See Bevilacqua F. 1993, pp. 324-5.

<sup>27</sup> Rankine M. 1853a, in Rankine M. 1881, p. 318.

thermodynamic processes: transformation of heat into macroscopic mechanical work, and the free flow of heat. They corresponded to the generalisation of Carnot and Fourier's theories respectively. When Rankine wrote his paper on Energetics, the two theories represented the two sections of the theory of heat which W. Thomson had tried to unify under the concept of "dissipation". Rankine's unified interpretation of the two fundamental processes, namely transformations of actual energy into work, and "*equable diffusion* of actual energy", was synthesised by the key concept of "*irreversibility*". This concept corresponded to the natural tendency to the transfer of actual energy.

There is an analogy in respect to this property of *irreversibility*, between the diffusion of one kind of actual energy and certain irreversible transformations of one kind of actual energy to another, called by Professor William Thomson, "Frictional Phenomena" – viz., the production of heat by rubbing, and agitation, and by electric currents in a homogeneous substance at a uniform temperature.<sup>28</sup>

According to Rankine, dissipation of energy and transformations of energy in general had an intrinsic connection with the measure of time. He thought that the inquiry into the connection "between energy and time" was "an important branch of the science of energetics", although, "at present" he was "prepared to state on this subject" nothing more than a "DEFINITION OF EQUAL TIMES". He therefore stated that, "*under wholly similar circumstances*", equal time spans would mean "*the times in which equal quantities of the same kind of work are performed by equal and similar substances*". The "science of energetics" aimed at a re-interpretation "of physical phenomena in general": it was an "abstract theory", namely a general and universal theory, encompassing all physical phenomena. Alongside the confidence in the generality and universality of his physical theory, there was the awareness that scientific practice was a potentially endless enterprise. In the last lines of his paper, Rankine emphasised that the "subjects" of physical sciences were "boundless", and that "they never can, by human labours, be exhausted, nor the science brought to perfection".<sup>29</sup>

An abstract approach and wide-scope generalisations were also the hallmarks of J. 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 "such as all material systems are":

<sup>28</sup> Rankine M. 1855, in Rankine M. 1881, p. 227.

<sup>29</sup> Rankine M. 1855, in Rankine M. 1881, pp. 227-8.

Thermodynamics was 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 system “is capable of two different kinds of action upon external systems”, and the two functions “afford an almost equally simple criterion of equilibrium”.<sup>30</sup>

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

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

$$(\delta\eta)_{\varepsilon} \leq 0 \quad (1)$$

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

$$(\delta\varepsilon)_{\eta} \geq 0 \quad (2)^{31}$$

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.<sup>32</sup>

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

$$d\varepsilon = t d\eta - p dv,$$

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  $S_1, S_2, \dots S_n$  of which the mass is composed” change their mass. As a consequence, the energy  $\varepsilon$  of the homogeneous component of the system could also depend on the corresponding variable masses  $m_1, m_2, \dots m_n$ :

<sup>30</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 55-6.

<sup>31</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 56.

<sup>32</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 62.

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n,$$

where  $\mu_1, \mu_2, \dots \mu_n$  denoted “the differential coefficients of  $\varepsilon$  taken with respect to  $m_1, m_2, \dots m_n$ ”. In general, also “component substances which do not initially occur in the homogeneous mass considered” had to be taken into account. To the coefficients  $\mu_x$  Gibbs attributed the qualification of “potential for the substance  $S_x$ ”.<sup>33</sup>

In more complex systems, each homogeneous sub-set depended on the  $(n+2)$  variables  $t, v, m_1, m_2, \dots m_n$ , and the whole system depended on  $(n+2)v$ , wherein  $v$  was “the number of homogeneous parts into which the whole mass is divided”. The series of equations involving  $t, p$ , and  $\mu_1, \mu_2, \dots \mu_n$  contained exactly  $(v-1)(n+2)$  conditions among the  $(n+2)v$  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”.<sup>34</sup> 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.

When the substances  $S_1, S_2, \dots S_n$  were not “all independent of each other”, but some of them could “be formed out of others”, new conditions were required. If  $\Sigma_a, \Sigma_b, \Sigma_k \dots$  denoted the units of certain substances  $S_a, S_b, S_k \dots$  among the  $S_1, S_2, \dots S_n$ , which underwent qualitative transformation, a new kind of “qualitative as well as quantitative equivalence” had to be satisfied:

$$\alpha \Sigma_a + \beta \Sigma_b + \text{etc.} = \kappa \Sigma_k + \lambda \Sigma_l + \text{etc.}^{\text{35}}$$

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

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

Under specific conditions, the functions  $\psi, \chi$ , and  $\zeta$  assumed specific meanings, and led to new conditions of equilibrium.

The quantity  $\psi$  has been defined for any homogeneous mass by the equation

<sup>33</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 63-5.

<sup>34</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 66.

<sup>35</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 67-9.



$$\psi = \varepsilon - t\eta.$$

We may extend this definition to any material system whatever which has a uniform temperature throughout.

If we compare two states of the system of the same temperature, we have

$$\psi' - \psi'' = \varepsilon' - \varepsilon'' - t(\eta' - \eta'').$$

If we suppose the system brought from the first to the second of these states without change of temperature and by a reversible process in which  $W$  is the work done and  $Q$  the heat received by the system, then

$$\varepsilon' - \varepsilon'' = W - Q,$$

and

$$t(\eta'' - \eta') = Q.$$

Hence

$$\psi' - \psi'' = W;$$

and for an infinitely small reversible change in the state of the system, in which the temperature remains constant, we may write

$$-d\psi = dW.^{36}$$

The function  $\psi$  represented “the force function of the system for constant temperature”, in brief the mechanical work done, “just as  $-\varepsilon$  is the force function for constant entropy”. In transformations with equal temperature in the initial and final states, the function  $\psi$  played the role of the internal energy  $\varepsilon$ , and the condition of equilibrium became

$$(\delta\psi)_t \geq 0.$$

Gibbs showed that the function  $\zeta$  played a similar role in transformations maintaining equal temperature and pressure in their initial and final states, so that

$$(\delta\zeta)_{t,p} \geq 0$$

Also the function  $\chi$  could assume a specific meaning under specific conditions: when “the pressure is not varied”,

$$d\chi = d\varepsilon + p dv = dQ - dW + p dv = dQ.$$

In other words, the function  $\chi$  could be qualified as “the *heat function for constant pressure*”, and its decrease represents “the heat given out by the system”. The system

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<sup>36</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 89.

underwent a purely thermal transformation, and in this case Gibbs also stressed the analogy with the internal energy  $\varepsilon$ , which “might be called the heat function for constant volume”.<sup>37</sup>

Gibbs was weaving the plot of a more general mechanics: he followed the track of Analytical Mechanics, but aimed at a wider-scope mechanics, which encompassed mechanics, thermodynamics and chemistry. 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  $\psi$  besides the functions  $\varepsilon$  and  $\eta$ , and the corresponding condition of equilibrium: when “the temperature of the system is uniform”, the condition of equilibrium could “be expressed by the formula”  $(\delta\psi)_t \geq 0$ . 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  $-\varepsilon$  and  $-\psi$  could “be regarded as a kind of force-function”, namely a generalisation of the concept of mechanical potential. The conditions of equilibrium  $(\delta\varepsilon)_\eta \geq 0$  and  $(\delta\psi)_t \geq 0$  would represent “extensions of the criterion employed in ordinary statics to the more general case of a thermodynamic system”.<sup>38</sup>

On the European Continent, other scholars pursued a phenomenological and macroscopic approach to Thermodynamics, which set aside specific mechanical models. In 1880, when the young Max Planck published the dissertation *Gleichgewichtszustände isotroper Körper in verschiedenen Temperaturen*, in order to be given the *venia legendi*, he outlined a mathematical theory where the mechanics of continuous media merged with thermal processes. In particular, when he made reference to forces “which act inside” isotropic bodies, he called into play the theory of elasticity and Thermodynamics. He reminded the reader that, in the former, temperature had been “tacitly assumed as constant”, and no connection between internal forces and temperature had been taken into account. On the contrary, in his essay, the role of temperature was to be considered explicitly, in particular “the influence of temperature on elastic forces inside bodies”. He relied on the two principles of “the mechanical theory of heat”, and “specific assumptions on the molecular structure (Beschaffenheit) of bodies” were

<sup>37</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89-91.

<sup>38</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 354-5. 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 C. 1984, p. 20). The same concept is re-stated in Truesdell C. 1986, p. 104. Nevertheless Truesdell appreciated Gibbs’ stress on entropy. See Truesdell C. 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.”

“not necessary”. In accordance with this theoretical option, he assumed that isotropic bodies consisted of “*continuous matter*”.<sup>39</sup>

Two years later, in the paper “Verdampfen, Schmelzen und Sublimieren”, Planck 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.<sup>40</sup>

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 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”.<sup>41</sup>

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

<sup>39</sup> Planck M. 1880, p. 1. 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. See McCormach R. and Jungnickel C. 1986, vol. 2, pp. 51-2, 152, and 254, and Gillispie C.C. (ed.), Volume XI, p. 8.

<sup>40</sup> Planck M. 1882, pp. 452 and 472. 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). Planck 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. See Kuhn T.S. 1987, p. 22. Similar remarks can be found in the book on the foundation of Thermochemistry Planck published in 1893.

<sup>41</sup> 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. For a brief scientific biography, see Cahan D. 1993b, p. 3. For a general account of Helmholtz’s contributions to Thermodynamics and Thermo-Chemistry, see Bierhalter G. 1993, and Kragh H. 1993.

indefinitely convertible into an equivalent amount of work, according to Clausius' interpretation of the Carnot law.

Die bisherigen Untersuchungen über die Arbeitswerthe chemischer Vorgänge beziehen sich fast ausschliesslich auf die bei Herstellung und Lösung der Verbindungen auftretenden oder verschwindenden Wärmemengen. Nun sind aber mit den meisten chemischen Veränderungen Aenderungen des Aggregatzustandes und der Dichtigkeit der betreffenden Körper unlöslich verbunden. Von diesen letzteren aber wissen wir schon, dass sie Arbeit in zweierlei Form zu erzeugen oder zu verbrauchen fähig sind, nämlich erstens in der Form von Wärme, zweitens in Form anderer, unbeschränkt verwandelbarer Arbeit. Ein Wärmevorrath ist nach dem von Hrn. Clausius präciser gefassten Carnot'schen Gesetze nicht unbeschränkt in andere Arbeitsäquivalente verwandelbar; wir können das immer nur dadurch und auch dann nur theilweise erreichen, dass wir den nicht verwandelten Rest der Wärme in einen Körper niederer Temperatur übergehen lassen.<sup>42</sup>

Helmholtz confined himself to chemical processes going on without any external action, and tried to go beyond the ordinary interpretation of the link between heat and "chemical affinity". He did not identify the stronger release of heat with a stronger affinity, namely the tendency leading to the establishment of chemical bonds: the two things did not necessarily coincide. He had found that chemical actions could give birth to "other kinds of energy besides mere heat": even in chemical processes the separation between the two components heat and work had to be taken into account. The generalisation of that distinction led to the concepts of "free and bound energy". Processes taking place spontaneously in systems at rest and at constant temperature, without the help of external work, could only go on "in the direction of decreasing free energy": it was just the rate of free energy, and not that of "whole energy", which decided in what direction affinity operated. Starting from the second Principle of thermodynamics, and the concept of free energy, he tried to weave a unifying theoretical net involving thermal, chemical and electrodynamic processes.<sup>43</sup>

Helmholtz labelled  $\vartheta$  the absolute temperature, and  $p_\alpha$  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  $P_\alpha$  was the external force corresponding to the parameter  $p_\alpha$ , 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,

$$\int dQ = dU + \sum_\alpha (P_\alpha \cdot dp_\alpha),$$

<sup>42</sup> Helmholtz 1882, pp. 958-9. It is worth remarking that, since the 1860s, Thermo-Chemistry "rested on the Thomsen-Berthelot principle". According to that principle, chemical reactions "were accompanied by heat production", and in these processes "the most heat was produced". 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. See Kragh H. 1993, pp. 404 and 409.

<sup>43</sup> Helmholtz 1882, p. 960.

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

Hierin bezeichnet  $\mathfrak{J}$  das mechanische Aequivalent der Wärmeeinheit und  $P_{\alpha} \cdot dp_{\alpha}$  die ganze bei der Aenderung  $dp_{\alpha}$  zu erzeugende, frei verwandelbare Arbeit, welche theils auf die Körper der Umgebung übertragen, theils in lebendige Kraft der Massen des Systems verwandelt werden kann. Diese letztere ist eben auch als eine den inneren Veränderungen des Systems gegenüberstehende äussere Arbeit zu betrachten.<sup>44</sup>

Beside this generalisation of the first principle, Helmholtz put forward a similar generalisation of the second law. He defined the entropy  $S$  as  $dQ/\vartheta$ , 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:

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

and the physical equivalence led to the mathematical relations

$$\mathfrak{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \mathfrak{J} \cdot \frac{\partial S}{\partial p_{\alpha}} = \frac{1}{\vartheta} \cdot \left( \frac{\partial U}{\partial p_{\alpha}} + P_{\alpha} \right). \quad ^{45}$$

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

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

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

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

<sup>44</sup> Helmholtz 1882, pp. 966-7.

<sup>45</sup> Helmholtz 1882, p. 967.

According to Helmholtz, the function  $\mathcal{F}$  represented the potential energy or the “Ergal” in the thermodynamic context. The functions  $U$  and  $S$  could be derived from  $\mathcal{F}$  by simple derivation:

$$\frac{\partial \mathcal{F}}{\partial \vartheta} = -\mathfrak{J} \cdot S, \text{ and } U = \mathcal{F} + \mathfrak{J} \cdot \vartheta \cdot S \text{ or } U = \mathcal{F} - \vartheta \cdot \frac{\partial \mathcal{F}}{\partial \vartheta}.$$

The function  $\mathcal{F}$  also represented the “free energy”, namely the component of the internal energy which could be transformed into every kind of work. If  $U$  represented the total internal energy, the difference between  $U$  and  $\mathcal{F}$ , namely  $\mathfrak{J} \cdot \vartheta \cdot S$ , represented the “bound energy”, namely the energy stored in the system as a sort of *entropic* heat.<sup>46</sup>

Helmholtz’s *mechanical* approach to Thermodynamics was 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. He tried to give a microscopic explanation of heat, without any recourse to specific mechanical models. This point deserves to be mentioned: in 1884, in the paper “Principien der Statik monocyklischer Systeme”, Helmholtz followed an intermediate pathway, which was neither Boltzmann nor Massieu-Gibbs’ pathway. He introduced a 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.<sup>47</sup>

Different *mechanical* theories of heat were on the stage in the last decades of the nineteenth century, and different meanings of the adjective *mechanical* were at stake.

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<sup>46</sup> Helmholtz 1882, pp. 968-9 and 971. As I have shown, the last two equations had already been derived from the French engineer Massieu: Helmholtz did not seem aware of Massieu’s result, which had probably not crossed the France borderlines.

<sup>47</sup> Buchwald stressed that Helmholtz put forward an Analytical-Mechanical approach to the microscopic level “without simultaneously adopting a fully reductionist atomism” (Buchwald J.Z. 1993, pp. 335). See also Cahan D. 1993b, p. 10. For a detailed analysis of Helmholtz’s 1884 paper, and similar theoretical researches which appear in the sixth volume of his *Vorlesungen über Theoretische Physik*, see Bierhalter G. 1993, pp. 437-42.

### 3. Duhem's Third Pathway: from Thermodynamic Potentials to "General Equations"

In 1886, the young Duhem published a book whose complete title was *Le potentiel thermodynamique et ses applications à la mécanique chimique et à l'étude des phénomènes électriques*. The content of the book corresponded to the doctoral dissertation he had submitted to the faculty late in 1884, before having achieved the *aggregation* in physics. This was an unusual procedure, but the faculty let the talented student present his dissertation, which however was rejected because of the new theoretical approach to thermodynamics, and because of the criticism it contained about M. Berthelot's chemical theories.<sup>1</sup>

In the "Introduction", he remarked that ordinary mechanics could not solve problems concerning chemical equilibrium, although those problems exhibited "several analogies with equilibrium problems in statics". According to Duhem, "*les physiciens*" should have made use of procedures similar to those used by "*les mécaniciens*" in the context of statics. We find here two meta-theoretical features of his scientific enterprise: his commitment to widen the scope of Mechanics, and, at the same time, his trust in the formal structure of Analytical Mechanics. A new generalised mechanics could bridge the gap between physics and chemistry through a generalisation of "the principle of virtual velocities and Lagrange's theorem". In accordance with his interests in the history of physics, Duhem briefly marshalled the theoretical contributions to thermodynamics and thermo-chemistry put forward by M. Berthelot, A. Horstmann, and W. Strutt (Lord Rayleigh) in the 1870s. He mentioned, in particular, Massieu's "characteristic functions"  $H$  and  $H'$ , and his derivation of some "physical and mechanical properties of bodies". Massieu's characteristic functions involved energy and entropy, the most meaningful entities in thermodynamics: the first function depended on temperature and volume, and the second on temperature and pressure.<sup>2</sup>

Duhem recollected the main steps of Gibbs' logical pathway: he listed Gibbs' potentials  $\psi = E(U - TS)$  and  $\zeta = E(U - TS) + pv$ , which were quite similar to Massieu's functions, and Gibbs' laws of equilibrium involving energy and entropy. He also mentioned Helmholtz's "distinction between two kinds of energy, the free energy ... and the bound energy": Helmholtz's free energy  $F$  was nothing else but Gibbs' function  $\psi$ , which in its turn was proportional to Massieu's "fonction caractéristique"  $H$ :  $F = E(U - TS) = \psi = -EH$ .<sup>3</sup>

Duhem wrote the first principle of Thermodynamics as

$$dQ + A d \sum \frac{mv^2}{2} = -dU + A d\tau_e,$$

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<sup>1</sup> Historians have set a link between Duhem's criticism of Berthelot and G.J. Lippmann's theories, on the one hand, and the impossibility of being appointed to a chair in Paris. Some letters received and sent by Duhem let this link emerge. See Brouzeng P. 1981b, pp. 141-51 and 169-71. For the events related to Duhem's dissertation, see Jaki S.L. 1984, pp. 50-2.

<sup>2</sup> Duhem P. 1886, pp. I-V. The expression "*les propriétés physiques et mécaniques*" cast some light upon the relationship between "physics" and "mechanics" in Duhem's view: physics encompassed the set of physical sciences outside Mechanics.

<sup>3</sup> Duhem P. 1886, pp. VI and IX. Physical remarks and historical reconstructions are tightly linked to each others: it is one of the long-lasting hallmarks of Duhem's scientific practice. The coefficient  $E$  was nothing else but "l'équivalent mécanique de la chaleur". The relationship between the mechanical equivalent of heat  $E$  and the thermal equivalent of mechanical work  $A$  is of course  $EA = 1$ .

where  $dQ$  was a quantity of heat,  $A d \sum \frac{mv^2}{2}$  the variation of living force,  $d\tau_e$  the variation of the external work,  $A$  the thermal equivalent of the mechanical work, and  $dU$  represented “the total differential of a function well specified apart from a constant”. With regard to the second principle, Duhem reminded the reader of Clausius’ interpretation of  $dQ/T$  as “*unit of transformation* or merely *transformation*”, and the corresponding theorem, “[t]he sum of transformations throughout a close eversible cycle is nought”. Then he reminded the reader of the extension of Clausius’ theorem to reversible “transformations different from a closed cycle”: the integral  $\int dQ/T$  depended “only on the initial and final state of the system”. Subsequently Clausius had included non-reversible closed cycles, which had led to a more general statement “[t]he algebraic sum of transformations occurring in a non-reversible closed cycle must be positive”. Including “whatever series of non-reversible transformations”, he had further widened the scope of the principle: the key concept was the “*non-compensated transformation*”. If a physical system passed from the initial state (0) to the final state (1) through different steps, one of them being at least non-reversible, and then came back to (0) through a series of reversible (r) steps,

$$\int \frac{dQ}{T} > 0 \quad \text{namely} \quad \int_0^1 \frac{dQ}{T} + \int_{(r) 1}^0 \frac{dQ}{T} > 0.$$

Making use of the definition of entropy  $\int_{(r) 1}^0 \frac{dQ}{T} = S_1 - S_2$ , Duhem reported Clausius’ result as

$$\int_0^1 \frac{dQ}{T} + S_1 - S_2 = N > 0.$$

On the track of Clausius’ theoretical pathway, Duhem qualified  $N$  as “*the sum of non-compensated transformations*”. In the specific case of isothermal transformations, he could write (5)  $N = A(\tau/T)$ , where  $\tau$  could be interpreted as “an amount of work which can be naturally qualified as *non-compensated work*”.<sup>4</sup>

These concepts emphasised the formal analogy between Mechanics and Thermodynamics.

*Aucune modification isothermique ne peut correspondre à un travail non compensé négatif.*

*Si une modification isothermique correspond à un travail non compensé positif, elle est possible, mais non réversible.*

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<sup>4</sup> Duhem P. 1886, pp. 3-7. It is worth noticing that Duhem labelled “principle” rather “theorem” Clausius’ statement about entropy or “transformation”, which corresponded to the second principle of thermodynamics. It is also worth noticing that the word “transformation” assumed two different meanings in Duhem’s paper: the general meaning of “change”, and the specific meaning of “entropy”.



*Pour qu'une modification isothermique soit réversible, il faut et il suffit que le système qui subit cette modification n'effectue aucun travail non compensé.*

*Un système est certainement en équilibre si l'on ne peut concevoir aucune modification isothermique de ce système qui soit compatible avec les liaisons auxquelles ce système est assujéti et qui entraîne un travail non compensé positif.*

Ces théorèmes rappellent, par leur forme et par leur objet, le principe des vitesses virtuelles. En thermodynamique, le travail non compensé joue, à certains points de vue, le même rôle que le travail en mécanique.<sup>5</sup>

For systems without any macroscopic living force, the first Principle became  $dQ = -dU + A d\tau_e$ , and for isothermal transformations, the other equations became

$$\tau = ETN \quad \text{and} \quad N = S_1 - S_0 + \frac{1}{T} \int_0^1 dQ.$$

A new mathematical expression for the non-compensated work  $\tau$  followed:

$$\tau = ET(S_1 - S_0) - E(U_1 - U_0) + \int_0^1 d\tau_e.$$

If external forces stemmed "from a potential  $W$ ", the last equation became

$$\tau = ET(S_1 - S_0) - E(U_1 - U_0) + W_0 - W_1,$$

and Duhem could define a more general potential  $\Omega = E(U - TS) + W$ . The very synthetic expression  $\tau = \Omega_0 - \Omega_1$  (8) followed: in his words, "non-compensated work ... is equal to the opposite of the variation of  $\Omega$ " in an isothermal transformation. The analogy between mechanics and thermodynamics led Duhem to choose the name "*thermodynamic potential of the system*" for the function  $\Omega$ .<sup>6</sup>

The previous statements concerning reversibility and equilibrium could be expressed in terms of the new potential.

*Il n'existe pas de modification isothermique ayant pour effet d'accroître le potentiel thermodynamique du système.*

<sup>5</sup> Duhem P. 1886, p. 7. In the following passage, Duhem specified the restrictions to be made on those statements: "Remarquons toutefois que le théorème de thermodynamique n'a pas exactement la même portée que le théorème de mécanique. Le principe des vitesses virtuelles indique les conditions nécessaires et suffisantes pour qu'un système soit en équilibre. Le théorème de thermodynamique indique que, dans certaines circonstances, un système demeure nécessairement invariable; on ne saurait prétendre que le système ne puisse rester invariable que dans ces conditions." Not only is this specification important in itself, but also for Duhem's subsequent theoretical researches in chemistry.

<sup>6</sup> Duhem P. 1886, pp. 7-8.

*Une modification isothermique qui a pour effet de faire décroître le potentiel thermodynamique du système est possible, mais non réversible.*

*Pour qu'une modification réversible soit réversible, il faut et il suffit que le potentiel thermodynamique demeure constant pendant toute la durée de cette modification.*

*Lorsque le potentiel thermodynamique est minimum, le système est dans un état d'équilibre stable.*<sup>7</sup>

In two specific instances, at constant volume or pressure, Duhem's thermodynamic potential had important consequences from the theoretical point of view, and from the point of view of "applications". In the first case,  $W = 0$ , and the potential  $\Omega$  became  $F = E(U - TS)$ , which was "Helmholtz's free energy" or Gibbs'  $\psi$  function. In the second case,  $dW = pdv = d(pv)$ , and the potential  $\Omega$  became  $\Phi = E(U - TS) + pv$ , which was "nothing else but Gibbs'  $\zeta$  function".<sup>8</sup>

The following section is definitely the most interesting from the point of view of the relationship between Mechanics and Thermodynamics. On the track of Massieu, Duhem expressed "all the parameters specifying the physical and mechanical properties of a system" in terms of the partial derivatives of  $F$  and  $\Phi$ . The function  $F$  had to be considered as a function of volume  $v$  and temperature  $T$ , whereas the function  $\Phi$  had to be considered as a function of pressure  $p$  and temperature. Duhem took into account a body "in a condition of equilibrium" and started from the two laws of Thermodynamics:

$$dS = -\frac{dQ}{T} \quad \text{and} \quad dQ = -(dU + A p dv).$$

Then he undertook a series of mathematical steps: he eliminated  $dQ$ , expressed  $S$  as a function of  $p$  and  $T$ , and computed the derivatives of the potential  $\Phi$  with regard  $p$  and  $T$ :

$$\frac{\partial \Phi}{\partial T} = -ES \quad \text{and} \quad \frac{\partial \Phi}{\partial p} = v.$$

Entropy and volume could be expressed as derivatives of the potential  $\Phi$ , and this result allowed Duhem to undertake the second step: the deduction of some mechanical and thermal properties of the system. He expressed "the coefficient  $\alpha$  of dilatation under constant pressure", "the coefficient  $\varepsilon$  of compressibility", and "the coefficient  $\alpha'$  of dilatation under constant volume" in terms of derivatives of the potential  $\Phi$ . Even specific heat at constant pressure was expressed in terms of the derivatives of the potential  $\Phi$ :

$$(19) \quad C = \frac{\partial U}{\partial T} + Ap \frac{\partial v}{\partial T} = A \left( -T \frac{\partial^2 \Phi}{\partial T^2} - p \frac{\partial^2 \Phi}{\partial T \partial p} \right) + Ap \frac{\partial}{\partial T} \frac{\partial \Phi}{\partial p} = -AT \frac{\partial^2 \Phi}{\partial T^2}.$$
<sup>9</sup>

<sup>7</sup> Duhem P. 1886, p. 9.

<sup>8</sup> Duhem P. 1886, pp. 9-10.

<sup>9</sup> Duhem P. 1886, pp. 10-13. There are some misprints in Duhem's text.

The general meaning of this achievement was stressed by Duhem at the end of the section.

Ainsi tous les coefficients qu'il est utile de connaître dans l'étude thermique d'un corps peuvent s'exprimer au moyen de  $\Phi$  et de ses dérivées premières et secondes par rapport à la pression et à la température, pourvu que l'on suppose le corps placé dans un état d'équilibre.<sup>10</sup>

In 1888 Duhem, at that time *Maitre de Conférences* in the Faculty of Science of Lille University, was allowed to discuss his new dissertation, *L'aimantation par influence*, in the Paris faculty of Science. He was awarded "*Docteur ès Sciences Mathématiques*" by an authoritative academic board: the president was the mathematician Gaston Darboux, and the examiners were H. Poincaré, then professor of probability calculus and mathematical physics, and Edmond Bouty, professor of physics. It is worth remarking that Duhem's second dissertation, its title and content notwithstanding, was presented in the class of mathematics rather than in the class of physics. In the meanwhile Duhem had published many papers on various subjects involving electromagnetism, thermo-electricity, thermo-chemistry, capillarity, osmosis, and phenomena dealing with vapours and chemical solutions.<sup>11</sup>

In accordance with a theoretical approach which borrowed words, concepts and procedures from Analytical Mechanics, Duhem followed Gibbs in stating that "the formal expression of the thermodynamic potential" was the first step towards the "determination of equilibrium for whatsoever system". Analytical Mechanics became a specific instance of a more general mechanics, wherein temperature and "chemical state" were as important as pure mechanical quantities. The usual physical quantities, like shape, position and velocities, could account for the displacement of a physical system, but could not account for its transformations or "change of state".

Pour connaître complètement l'état du système, il faudra connaître la position de l'origine de chacun de ces systèmes d'axes et l'orientation des axes. En général, il faut aussi connaître un certain nombre d'autres quantités : forme et volume, état physique et chimique dans lequel il se trouve, température qu'il possède en ses divers points, etc. Lorsque les premières quantités varieront seules, les autres demeurant invariables, nous dirons que *l'on déplace les uns par rapport aux autres les divers corps du système sans changer leur état*.<sup>12</sup>

Although the keystone of that re-interpretation of Thermodynamics, namely "the uncompensated work", was a concept which "it would be vain to look for" in ordinary mechanics, Duhem saw a deep conceptual link "tying Mechanics to Thermodynamics". In

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<sup>10</sup> Duhem P. 1886, p. 13. A further series of mathematical steps allowed Duhem to express the above coefficients in terms of the first and second derivatives with regard to  $v$  and  $T$  of the potential function  $F$ . See *Ibidem*, p. 13: "On pourrait montrer d'une manière analogue que si l'on a soin d'exprimer la fonction  $F$  au moyen des variables  $v$  et  $T$ , les dérivées partielles de cette fonction permettent d'exprimer tous les coefficients dont la connaissance est utile dans l'étude thermique ou mécanique du corps."

<sup>11</sup> The word "thermodynamics", which would have upset influential scientists like Berthelot and G.J. Lippmann, did not appear in the title of Duhem's second dissertation. For further details, see Jaki S.L. 1984, pp. 78-9, and 437-9. For a complete bibliography of Duhem's scientific, historical and philosophical works, see Manville O. 1927, pp. 437-64, and Jaki S.L. 1984, pp. 437-55. For an essential chronology of Duhem's life, see Brouzeng P. 1987, pp. 161-5.

<sup>12</sup> Duhem P. 1888, p. 5.

particular, he tried to deduce the Principle of virtual velocities from “the fundamental principle of Thermodynamics”. In the specific case of “rational Mechanics”, stable equilibrium was assured by the following statement:

*L'équilibre d'un système dont les diverses parties sont susceptibles de se déplacer, mais non d'éprouver des changements d'état, est assuré si le travail effectué dans tout déplacement virtuel de ce système par toutes les forces qui agissent sur lui est nul ou négatif.*

[...]

*L'équilibre stable d'un système soumis à des forces extérieures qui admettent un potentiel est assuré lorsque le potentiel total des forces, tant intérieures qu'extérieures, est minimum.<sup>13</sup>*

A “slight difference” separated Thermodynamics from Mechanics: the key point was equilibrium, in particular the necessary and sufficient conditions for equilibrium. In pure Mechanics the principle of virtual velocities was both a necessary and a sufficient condition for mechanical equilibrium. In Thermodynamics, the second Principle was a sufficient but not necessary condition for equilibrium. A physical system could not experience “a change of state contrary to Carnot-Clausius’ principle”: if the virtual transformations of the system “opposed that principle, the system would be inevitably in equilibrium”. Nevertheless, if the system experienced “a virtual transformation consistent with that principle, we do not know whether that transformation will really take place or not”.<sup>14</sup>

That subtle difference could be traced back to the foundations of Mechanics. Even in “mechanical”, but not *purely* mechanical systems, when dissipative effects were at stake, equilibrium could persist when the principle of virtual velocities of rational Mechanics was not satisfied.

*J'ajouterai que le principe des vitesses virtuelles, présenté par la Thermodynamique comme condition suffisante, mais non nécessaire, de l'équilibre est toujours conforme à l'expérience, tandis que l'expérience nous présente chaque jour des cas d'équilibre contraires au principe des vitesses virtuelles tel qu'on l'admet en Mécanique rationnelle ; on dit alors qu'il y a *frottement*, et le principe des vitesses virtuelles suppose un système soumis à des liaisons dépourvues de frottement.<sup>15</sup>*

In the subsequent years, Duhem was to develop the structural analogy between Mechanics and Thermodynamics. In the last years of the 1880s, he began to specify his theoretical pathway: he pursued a very general theory, based on the two principles of Thermodynamics, and translated into the language of Analytical Mechanics, which led to differential equations more general than Lagrange’s.

After three years, while he was lecturing at Lille university, Duhem began to outline a systematic design of rephrasing Thermodynamics. He published a paper in the official revue of the *Ecole Normale Supérieure*, wherein he displayed what he called the “general equations

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<sup>13</sup> Duhem P. 1888, p. 12.

<sup>14</sup> Duhem P. 1888, pp. 12-13.

<sup>15</sup> Duhem P. 1888, p. 13.

of Thermodynamics". Once again 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": F. Massieu, J.W. Gibbs, H. von Helmholtz, and A. von 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".<sup>16</sup>

In the first section, "Étude 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  $\vartheta$  and  $n$  other independent quantities  $\alpha$ ,  $\beta$ , ...,  $\lambda$ . He then introduced some "external forces", which depended on  $\alpha$ ,  $\beta$ , ...,  $\lambda$  and  $\vartheta$ , 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:

$$A = f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta)$$

$$B = f_\beta(\alpha, \beta, \dots, \lambda, \vartheta)$$

.....

$$L = f_\lambda(\alpha, \beta, \dots, \lambda, \vartheta)$$

$$\Theta = f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta).^{17}$$

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 parameters:

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

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

<sup>16</sup> Duhem P. 1891, pp. 231-2. 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.

<sup>17</sup> Duhem P. 1891, p. 233-4.

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

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

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 new alliance between Mechanics and Thermodynamics led to a sort of symmetry between thermal and mechanical quantities. The  $n+1$  functions  $R_\alpha, R_\beta, \dots, R_\lambda, R_\vartheta$ , which Duhem re-wrote as  $R_\alpha, R_\beta, \dots, R_\lambda, C$ , played the role of *generalized thermal capacities*, and the last term  $C$  was nothing else but the ordinary thermal capacity: in some way, the second typographical choice re-established the traditional asymmetry.<sup>18</sup>

In the following pages Duhem inquired into the connection between the mathematical and physical aspects of the principle of equivalence. Starting from the first and second Principles of Thermodynamics, he arrived at the equations

$$\frac{\partial R_\alpha}{\partial \beta} - \frac{\partial R_\beta}{\partial \alpha} = - \frac{1}{E} \left( \frac{\partial A}{\partial \beta} - \frac{\partial B}{\partial \alpha} \right)$$

$$\frac{\partial R_\alpha}{\partial \vartheta} - \frac{\partial C}{\partial \alpha} = - \frac{1}{E} \left( \frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right).$$

The physical *equivalence* between work and heat was transformed into a mathematical *equivalence* between their  $n+1$  differential coefficients, namely the series of functions  $A, B, \dots, L, \Theta$ , and the series  $R_\alpha, R_\beta, \dots, R_\lambda$ . The mathematical equivalence expressed by the last equations required the existence of a function of state  $U$ , namely “a uniform function of  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ , so that  $E(dQ + dU) = d\tau_e$ ”. Coming back to the physical point of view, the mathematical equivalence corresponded to “the principle of equivalence between work and heat”.<sup>19</sup>

Another set of equations proved to be useful in the building up of Duhem’s Thermodynamics. The Lagrangian parameter  $\vartheta$  could be chosen without any restriction: it did not have to be necessarily identified with the absolute temperature. In general, the absolute temperature could be a function  $F(\vartheta)$  of  $\vartheta$ . This means that the function entropy, a “uniform, finite, and continuous function of  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ ”, had to be defined as

<sup>18</sup> Duhem P. 1891, p. 234.

<sup>19</sup> Duhem P. 1891, p. 235.

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

$$-\frac{R_\alpha}{F(\vartheta)} \cdot \delta\alpha - \frac{R_\beta}{F(\vartheta)} \cdot \delta\beta - \dots - \frac{R_\lambda}{F(\vartheta)} \cdot \delta\lambda - \frac{R_\vartheta}{F(\vartheta)} \cdot \delta\vartheta.$$

New mathematical equivalences could be derived:

$$\frac{\partial}{\partial\beta} \frac{R_\alpha}{F(\vartheta)} = \frac{\partial}{\partial\alpha} \frac{R_\beta}{F(\vartheta)}, \text{ or } \frac{1}{F(\vartheta)} \left( \frac{\partial R_\alpha}{\partial\beta} - \frac{\partial R_\beta}{\partial\alpha} \right) = 0,$$

$$\frac{1}{F(\vartheta)} \left( \frac{\partial R_\alpha}{\partial\vartheta} - \frac{F'(\vartheta)}{F(\vartheta)} R_\alpha \right) = \frac{1}{F(\vartheta)} \frac{\partial C}{\partial\alpha}.^{20}$$

Even in this case, the mathematical and physical steps could be reversed. The mathematical equivalence expressed by the last equations required the existence of a function of state  $S$ , namely "a uniform function  $S$  of the state of the system"  $dS = dQ/F(\vartheta)$ . In the context of the generalised theory, the functions internal energy  $U$  and entropy  $S$  also emerged as two basic state-functions.

*Prenons un système dont l'équilibre est assuré par des forces ayant pour travail virtuel la quantité*

$$d\tau_e = A \cdot \delta\alpha + B \cdot \delta\beta + \dots L \cdot \delta\lambda + \Theta \cdot \delta\vartheta,$$

*et dans lequel une transformation élémentaire à partir d'un état d'équilibre dégage une quantité de chaleur*

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

*pour que ce système vérifie les deux principes fondamentaux de la Thermodynamique, il faut et il suffit que les deux quantités*

$$\left( R_\alpha + \frac{A}{E} \right) \cdot \delta\alpha + \left( R_\beta + \frac{B}{E} \right) \cdot \delta\beta + \dots \left( R_\lambda + \frac{L}{E} \right) \cdot \delta\lambda + \left( C + \frac{\Theta}{E} \right) \cdot \delta\vartheta,$$

$$\frac{R_\alpha}{F(\vartheta)} \cdot \delta\alpha + \frac{R_\beta}{F(\vartheta)} \cdot \delta\beta + \dots \frac{R_\lambda}{F(\vartheta)} \cdot \delta\lambda + \frac{R_\vartheta}{F(\vartheta)} \cdot \delta\vartheta$$

*soient deux différentielles totales.<sup>21</sup>*

The two series of mathematical equivalences had an important consequence from both the mathematical and physical points of view. In fact, they led to a series of equations of the kind

<sup>20</sup> Duhem P. 1891, pp. 235-6. Here a sort of asymmetry between *mechanical* and *thermal* parameters emerges.

<sup>21</sup> Duhem P. 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.

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

As Duhem remarked, this equation says that the  $n+1$  functions  $f_\alpha, f_\beta, \dots, f_\lambda$ , and  $f_\vartheta$ , which define the differential coefficients  $A, B, \dots, L$ , and  $\Theta$ , “could not be chosen arbitrarily”. In particular it suggests that “a uniform, finite, and continuous function  $\mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta)$  of  $n+1$  parameters  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$  there exist”. The gradient of  $\mathcal{F}$  can be written component by component, taking care of the specific behaviour of the component  $\Theta$ , which was “independent of the function  $\mathcal{F}$ ”:

$$A = \frac{\partial}{\partial \alpha} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta), B = \frac{\partial}{\partial \beta} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta), \dots L = \frac{\partial}{\partial \lambda} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta).^{22}$$

What do we know about the functions  $\Theta$  and  $R_\vartheta = C$ , which could not be derived by the same procedure? The knowledge of the “equilibrium equations of a system” allowed Duhem to compute the partial derivatives of the thermal capacity  $C$  with regard to all the parameters which described the state of the system, “apart from its derivative with regard to temperature”. The thermal capacities were therefore known “except for an unspecified function of temperature”:

$$(9) \frac{\partial C}{\partial \alpha} = \frac{1}{E} \left\{ \left( \frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right) \left[ 1 - \frac{\partial F(\vartheta)}{\partial \vartheta F'(\vartheta)} \right] - \frac{F(\vartheta)}{F'(\vartheta)} \left( \frac{\partial^2 A}{\partial \vartheta^2} - \frac{\partial^2 \Theta}{\partial \alpha \partial \vartheta} \right) \right\}, \frac{\partial C}{\partial \beta} = \dots, \dots, \frac{\partial C}{\partial \lambda} = \dots$$

The last set of equations shows how deeply entangled were the *thermal* and *mechanical* properties of a physical system.<sup>23</sup>

The complex net of equations developed by Duhem could be simplified by an appropriate choice of Lagrangian parameters: the choice of the absolute temperature as thermal parameter, namely  $\vartheta = T$  and  $F(T) = T$ , let simpler expressions for  $C$  derivatives emerge. A further simplification could be attained by choosing the parameters  $\alpha, \beta, \dots$ , and  $\lambda$  in order to keep at rest the whole system when the parameter  $\vartheta$  changed. In this case, “the mere change of  $\vartheta$  cannot involve any work done by external forces”, and a sort of split between thermal and mechanical features of the system was imposed. Nevertheless, the existence of mathematical links between the *mechanical* derivatives of the *thermal* scalar  $C$  and the *thermal* derivatives of the generalised *mechanical* vector  $(A, B, \dots, L)$  shows us the persistence of the deep connection between mechanical and thermal effects, even when the formal symmetry between them was weakened:

<sup>22</sup> Duhem P. 1891, pp. 237-8. In terms of vector calculus, if  $\mathbf{K} = (A, B, \dots, L)$  and  $\nabla \times \mathbf{K} = 0$ , then  $\mathbf{K} = \nabla \mathcal{F}$ , just because  $\nabla \times \nabla \mathcal{F} = 0$  for every  $\mathcal{F}$ .

<sup>23</sup> Duhem P. 1891, pp. 238-9.



$$\frac{\partial C}{\partial \alpha} = -\frac{T}{E} \frac{\partial^2 A}{\partial T^2}, \quad \frac{\partial C}{\partial \beta} = -\frac{T}{E} \frac{\partial^2 B}{\partial T^2}, \dots, \dots, \quad \frac{\partial C}{\partial \lambda} = -\frac{T}{E} \frac{\partial^2 L}{\partial T^2}.^{24}$$

According to Duhem, "the mechanical determination of the system" required firstly the specification of the function  $\mathcal{F}$ , and then the deduction of the generalized forces  $A, B, \dots, L$ , and  $\Theta$ , and the "thermal coefficients"  $R_\alpha, R_\beta, \dots$ , and  $R_\lambda$ . Duhem's 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 had accomplished the design outlined in 1886: the derivation of mechanical and thermal features of the system from the potential  $\mathcal{F}$  and the function  $\Theta = f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta)$ .

On voit donc que, si l'on connaît le potentiel thermodynamique interne d'un système et si l'on connaît en outre la fonction  $f_\vartheta$ , on sait déterminer les conditions d'équilibre du système, l'énergie, l'entropie et les coefficients calorifiques du système en équilibre, en sorte que l'étude mécanique et thermique du système en équilibre est complète.<sup>25</sup>

In the last section of his 1891 paper, "D'un changement de variable", Duhem outlined an alternative analytic approach to thermodynamics. He had followed a procedure which, starting from the configuration of the system, corresponding to the choice of the  $n+1$  parameters  $\alpha, \beta, \dots, \lambda$  and  $\vartheta$ , had led to the equations of equilibrium for the  $n+1$  functions  $A, B, \dots, L$ , and  $\Theta$ , and the  $n+1$  functions  $R_\alpha, R_\beta, \dots, R_\lambda$ , and  $R_\vartheta$ . That procedure could be reversed: instead of starting from the *geometrical-thermal* parameters  $\alpha, \beta, \dots, \lambda$  and  $\vartheta$ , in order to arrive at the *dynamical* conditions of equilibrium for  $A, B, \dots$ , and  $L$ , he showed that he could start from the *dynamical-thermal* parameters  $A, B, \dots, L$ , and  $\vartheta$ , in order to arrive at the *geometrical* equations of equilibrium on  $\alpha, \beta, \dots$ , and  $\lambda$ .<sup>26</sup>

In Duhem's representation, physical events took place in a sort of abstract hyper-space at  $n+1$  components:  $n$  *mechanical* components  $\alpha, \beta, \dots$ , and  $\lambda$ , and one *thermal* component  $\vartheta$ . The Lagrangian representation of phenomena in space and time required  $n$  generalized parameters  $\alpha, \beta, \dots$ , and  $\lambda$ , and time  $t$ . In the tradition of mechanics, the parameter  $t$  played a double role: it was both an explicit parameter, which could be placed alongside the spatial parameters, and a basic parameter, which spatial parameters depended on. At that stage, Duhem did not take into account time as an explicit parameter; this role was played by the *thermal* parameter  $\vartheta$ .

From the 1880s onwards, Duhem had pursued a new alliance between Lagrangian mechanics and the science of heat, and that pursuit was not an isolated enterprise. In the same years, in Great Britain, G.F. FitzGerald, J.J. Thomson and J. Larmor were looking for a new

<sup>24</sup> Duhem P. 1891, pp. 239-41.

<sup>25</sup> Duhem P. 1891, p. 251. An unaccountable missing sign in the equation for entropy led Duhem to compute, in a relatively easy way, the expressions for  $U, S$  and  $C$ . The fact is that the mistaken sign makes the derivation too easy: the right computation leads to differential equations for  $U$  and  $S$ , which are not so easy to solve. The qualitative features of Duhem's design are not threatened by the wrong derivation, and its conclusion is qualitatively correct. Duhem's mistake stems from the difference between the definition  $dQ/F(\vartheta) = dS$  (p. 236) and the different definition  $\delta S = -dQ/F(\vartheta)$  (p. 251).

<sup>26</sup> Duhem P. 1891, pp. 259-61.

alliance between Lagrangian mechanics and the science of electromagnetic phenomena. A new kind of alliance between Analytical Mechanics and a field theory purified by the concept of force led Hertz to a bold design of the geometrization of physics in 1894.<sup>27</sup>

Duhem's design had a two-fold target: the unification of physics under the principles of thermodynamics, and the translation of that unified physics into a sophisticated mathematical language. The specific features of Duhem's design were quite different from the specific features of Boltzmann's design: if the latter had tried to give a *microscopic* mechanical explanation of the *macroscopic* laws of Thermodynamics, Duhem assumed those *macroscopic* laws as starting point. There is a great difference between their theoretical procedures indeed, even though we cannot find a great difference in their general perspectives. Both Boltzmann and Duhem exploited the tradition in which they had been trained, and led it to its ultimate consequences; at the same time, they dared to go far beyond that tradition.

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<sup>27</sup> Hertz's main aim was the reduction of all physics to a generalised new mechanics. 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". In the end, physics was reduced to mechanics and mechanics was reduced to geometry and kinematics. This new physics appeared in accordance with the theoretical model of contiguous action. See Hertz H. 1894, in Hertz H. 1956, "Author's Preface", p. 1, and p. 41.

#### 4. *The Generalised Mechanics of a “Complex System”*

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. From the first passages of the first paper a wide historical and philosophical perspective emerged: the history of science appeared as a periodical series of complementary trends of innovations and applications.

Toute science avance comme par une série d’oscillations.

A certaines époques, on discute les principes de la science ; on examine les hypothèses qu’ils supposent, les restrictions auxquelles ils sont soumis. Puis, pour un temps, ces principes semblent bien établis : alors les efforts des théoriciens se portent vers la déduction des conséquences ; les applications se multiplient, les vérifications expérimentales deviennent nombreuses et précises.

Mais ce développement, d’abord rapide et facile, devient par la suite plus lent et plus pénible ; le sol, trop cultivé, s’appauvrit ; alors surgissent des obstacles, que les principes établis ne suffisent pas à lever, des contradictions qu’ils ne parviennent pas à résoudre, des problèmes qu’ils sont incapables d’aborder. A ce moment, il devient nécessaire de revenir aux fondements sur lesquels repose la science, d’examiner à nouveau leur degré de solidité, d’apprécier exactement ce qu’ils peuvent porter sans se dérober. Ce travail fait, il sera possible d’édifier de nouvelles conséquences de la théorie.<sup>1</sup>

According to Duhem, in the last “thirty years”, many “applications” had stemmed from Thermodynamics: at that time, the end of the nineteenth century, a deep “reconsideration of the principles was needed”. Before developing his theoretical design, Duhem expressed some meta-theoretical cogitation, which he qualified as “more philosophical than mathematical”. The “logical order” of a physical theory could only rest upon “a certain number of definitions and hypotheses, which are, to some extent, arbitrary”. He acknowledged that different theoretical approaches to Thermodynamics could be “equally satisfactory, even more satisfactory” than his own: a plurality of theories could describe a given set of phenomena in a consistent way.<sup>2</sup>

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<sup>1</sup> Duhem 1892a, p. 269. Duhem’s representation of the history of science as a periodical series of plain applications and deep transformations has been subsequently exploited by historians of science. After seventy years, in a completely different intellectual context, Kuhn put forward a representation of the history of science as a periodical series of “normal” science and “revolutionary” stages. See, for instance, Kuhn T.S. 1962, in Kuhn T.S. 1996, pp. 10 and 111. Kuhn did not mention Duhem: the label *continuist* had already been stuck on Duhem’s shoulders. As Brenner remarked some years ago, “historiographical continuism can perfectly stay beside epistemological discontinuism” (Brenner A. 1992, p. XIX). Sometimes buried memories flow through the history and philosophy of science.

<sup>2</sup> Duhem 1892a, p. 270. I find it useful to quote Duhem’s complete passage: “Toute théorie physique repose sur un certain nombre de définitions et d’hypothèses qui sont, dans une certaine mesure, arbitraires ; il est donc permis de chercher à exposer une semblable théorie dans un ordre logique ; mais prétendre qu’on a lui donné le seul ordre logique dont elle soit susceptible serait une prétention injustifiable. Cette prétention, nous nous garderons bien de l’avoir. Nous sommes convaincu que l’ont peut enchaîner les principes de la Thermodynamique d’une manière autre que celle que nous avons adoptée et cependant aussi satisfaisante, plus satisfaisante peut-être. Nous n’oserions même espérer qu’aucune lacune ne subsiste dans l’enchaînement que nous avons cherché à établir.”

In the first chapter, “Définitions préliminaires”, which dealt with the geometrical and kinematical foundations of physics, the equivalence between different theoretical representations was stated once again. Duhem insisted on the arbitrariness of every hypothesis on the ultimate representation of matter, and stressed the equivalence between continuous and discontinuous models of matter. At the same time, he expressed explicitly his preference for theoretical models based on continuous distributions of matter.

*En Physique, il nous est à la fois impossible et inutile de connaître la constitution réelle de la matière. Nous cherchons simplement à concevoir un système abstrait qui nous fournisse une image des propriétés des corps. Pour construire ce système, nous sommes libres de représenter un corps qui nous semble continu soit par une distribution continue de matière dans un certain espace, soit par un ensemble discontinu d’atomes très petits. Le premier mode de représentation conduisant, dans toutes les parties de la Physique, à des théories plus simples, plus claires et plus élégantes, nous l’adopterons de préférence au second.*<sup>3</sup>

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  $A, B, \dots$ , and  $L$  the elements of the first set, and  $\alpha, \beta, \dots$ , and  $\lambda$  the elements of the second. Matter could be described geometrically by some functions of Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ : among state quantities Duhem distinguished those which appeared explicitly in those equations from those which did not appear. He reserved the labels  $\alpha, \beta, \dots$ , and  $\lambda$  for the former, and introduced new labels  $a, b, \dots, l$  for the latter: in some way he separated geometrical quantities from other quantities. He called “*virtual transformation*” the “purely intellectual procedure” representing the continuous series of steps leading from a specific initial state to a final state. 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  $\vartheta$ , any continuous and increasing function  $\Theta = f(\vartheta)$  could play the role of temperature.<sup>4</sup>

In the third chapter he started from a complex system  $\Sigma$ , which was isolated in space, and could be looked upon as the composition of two “independent systems”  $S$  and  $S'$ . If the

<sup>3</sup> Duhem 1892a, p. 272. Duhem remarked that, sometimes, some theoretical representations were unjustified from the empirical point of view. The concept of “an isolated body placed in an unlimited and empty space” was one of them. Nevertheless, those representations could be useful simplifications: physics could not part with those kinds of abstraction. (*Ibidem*, p. 274)

<sup>4</sup> Duhem 1892a, pp. 276, 278-9, 284 and 286-8. 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  $\vartheta$  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. (*Ibidem*, pp. 291-307)

kinetic energy of  $\Sigma$  was simply the sum of the kinetic energies  $\mathcal{T}$  and  $\mathcal{T}'$  of  $S$  and  $S'$ , the potential energy could not consist only of the sum of the two isolated potential energies  $U$  and  $U'$ , but had to contain a term of *interaction*:

$$Y = U(\alpha, \beta, \dots, \lambda; a, b, \dots, l) + U'(\alpha', \beta', \dots, \lambda'; a', b', \dots, l') \\ + \Psi(\alpha, \beta, \dots, \lambda; a, b, \dots, l; \alpha', \beta', \dots, \lambda'; a', b', \dots, l')$$

The total energy of  $\Sigma$  was  $\varepsilon = Y + (1/E)(\mathcal{T} + \mathcal{T}')$ , and generalised forces could be derived from the potential of interaction  $\Psi$ :

$$E \frac{\partial \Psi}{\partial \alpha} = -A, \quad E \frac{\partial \Psi}{\partial \beta} = -B, \dots, \quad \dots, \quad E \frac{\partial \Psi}{\partial \lambda} = -L, \\ E \frac{\partial \Psi}{\partial a} = -\mathcal{A}, \quad E \frac{\partial \Psi}{\partial b} = -\mathcal{B}, \dots, \quad \dots, \quad E \frac{\partial \Psi}{\partial l} = -\mathcal{L}$$

The first set corresponded to “*forces*”, and the second set to “*influences* exerted by the system  $S'$  on the system  $S$ ”: Duhem called “*actions*” the ensemble of forces and influences. The separation of actions into forces and influences followed necessarily from the separation of Lagrangian parameters into geometrical parameters and other state parameters. After having defined the generalized velocities

$$u = \frac{d\alpha}{dt}, \quad v = \frac{d\beta}{dt}, \quad \dots, \quad w = \frac{d\lambda}{dt}, \quad \text{and} \quad \varphi = \frac{da}{dt}, \quad \chi = \frac{db}{dt}, \quad \dots, \quad \psi = \frac{dl}{dt},$$

Duhem represented the work done by forces and influences as

$$(A \cdot u + B \cdot v + \dots + L \cdot w) dt \quad \text{and} \quad (\mathcal{A} \cdot \varphi + \mathcal{B} \cdot \chi + \dots + \mathcal{L} \cdot \psi) dt.^5$$

In the more complex case of three “partial systems  $S_1, S_2, S_3$ ”, the potential  $\Psi$  became the sum of three couples of interaction:  $\Psi = \Psi_{1-2} + \Psi_{2-3} + \Psi_{1-3}$ . In the following pages, Duhem generalized definitions and remarks to the case of a system  $\Sigma$  composed of “ $n$  independent systems  $S_1, S_2, \dots, S_n$ ”. Conversely, those definitions and remarks allowed Duhem to outline, at least in part, the features of a “complex system”.

<sup>5</sup> Duhem 1892a, pp. 308-9 and 311. Unfortunately, “forces” and parameters representing the “nature” of the system were labelled with the same letters. The potential of interaction  $\Psi$  deserved some additional mathematical and physical remarks. See Ibidem, pp. 312-13: “Ainsi le travail des actions du système  $S'$  sur le système  $S$  n'est pas, en général, une différentielle totale, mais le travail des actions mutuelles des deux systèmes  $S$  et  $S'$  est toujours la différentielle totale d'une fonction qui est définie d'une manière uniforme lorsqu'on connaît l'état du système  $\Sigma$  constitué par l'ensemble de deux systèmes  $S$  and  $S'$ . La fonction  $E\Psi$ , dont la différentielle totale, changée de signe, donne le travail des actions mutuelles des deux systèmes  $S$  et  $S'$ , se nomme le potentiel de ces actions.”

*Dans un système complexe, formé de plusieurs systèmes indépendants, chacun de ces derniers subit certaines actions de la part de l'ensemble des autres ; toutes ces actions, prises ensemble, admettent un potentiel.*

*Ce potentiel  $E\Psi$  dépend des propriétés des divers systèmes indépendants qui composent le système complexe, et de leur position relative ; il ne dépend pas de la position absolue que le système complexe occupe dans l'espace.<sup>6</sup>*

The key entity was the total energy

$$\varepsilon = Y + \frac{1}{E}(\mathcal{T} + \mathcal{T}') = U + U' + \Psi + \frac{1}{E}(\mathcal{T} + \mathcal{T}').$$

Heat had a relational nature: in a “complex isolated system, consisting of two independent systems S and S’, ... one of them sends out as much heat as the other receives”. The concept of an isolated body placed in an empty space, and sending out or receiving heat, seemed to Duhem “not consistent with the definition given above”. According to Duhem, heat meant exchange of heat: heat required interactions between different bodies, or at least between a body and the surrounding aether.<sup>7</sup>

Consistently with the separation between geometrical and “state” parameters, he introduced two sets of “thermal coefficients”,  $R_\alpha, R_\beta, \dots, R_\lambda$ , and  $\mathcal{R}_a, \mathcal{R}_b, \dots, \mathcal{R}_l$ , such that

$$E R_\alpha = \left( E \frac{\partial U}{\partial \alpha} - A \right) - \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right),$$

$$E \mathcal{R}_a = \left( E \frac{\partial U}{\partial a} - \mathcal{A} \right),$$

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

On the right-hand side of the last equation, the first bracket contains the effect of mechanical actions, and the second the effects of other kinds of *influences*: the latter was a generalization of the term  $R_\vartheta$  which Duhem had introduced in 1891. In Duhem’s words, those coefficients depended on “the properties of the system S”, on “velocities and accelerations” of every point of S, and on “the actions of the system S’ on S”. In reality, 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

<sup>6</sup> Duhem 1892, p. 315.

<sup>7</sup> Duhem 1892a, pp. 310 and 319-20. In the last part of the chapter, Duhem stressed his relational conception of heat once again. See p. 323: “Ici vient naturellement se placer une réflexion semblable à celle que nous a suggérée la définition du travail : on ne peut parler de la quantité de chaleur dégagée par chacune des parties d’un système qu’autant que chacune de ces parties peut être considérée comme un système indépendant. Lorsque les diverses parties d’un système ne sont pas indépendantes les unes des autres, le mot : quantité de chaleur dégagée par chacune d’elles n’a aucun sens.”

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

The last two sets of equations specified the terms which appeared in the fundamental equation  $E(dQ + \delta U) = d\tau$ , which was nothing else but the first principle of Thermodynamics or “the law of equivalence between heat and work”.<sup>8</sup>

Duhem’s generalised Mechanics/Thermodynamics was 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

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

$$E \frac{\partial U}{\partial a} - \mathcal{A} = 0, \dots \dots$$

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. Moreover, it is questionable whether the vanishing of the “thermal coefficients” and the condition  $dQ = 0$  are equivalent statements. At the end of Duhem’s 1892 paper, the nature of the formal relationship between Mechanics and Thermodynamics was waiting for a complete clarification.<sup>9</sup>

With regard to the foundations of Thermodynamics, we find a sort of intellectual dialogue between Duhem and Poincaré in the treatise which the latter devoted to the subject in 1892. Just like Duhem’s papers, essays and books, Poincaré’s treatise was a *treatise* in a very deep sense, for we find remarks on the foundations of physics, meta-theoretical cogitations, and historical reconstructions alongside detailed analyses of experiments, and their interpretations. Poincaré appreciated Duhem’s researches, even though he devoted some pages of his treatise to oppose Duhem’s interpretations of specific phenomena.<sup>10</sup> Poincaré

<sup>8</sup> Duhem 1892a, pp. 320-1.

<sup>9</sup> See Duhem P. 1892a, p. 324: “On voit que les lois de la Dynamique rentrent, comme cas particulier, dans les lois de la Thermodynamique ; elles se déduisent de ces dernières en supposant tous les coefficients calorifiques du système égaux à 0 ; mais dans quel cas cette hypothèse est-elle vérifiée? C’est une question qui reste à examiner et que rien, dans ce que nous avons dit jusqu’ici, ne permet de résoudre. Dans la plupart des cas, elle n’est résolue que par voie d’hypothèse, directe ou indirecte. D’ailleurs, nous verrons plus tard qu’il existe une autre manière, distincte de celle-là, de faire dériver les équations de la Dynamique des équations de la Thermodynamique.”

<sup>10</sup> See Poincaré H. 1892, p. XIX: “J’ai eu deux fois l’occasion d’être en désaccord avec M. Duhem ; il pourrait s’étonner que je ne le cite que pour le combattre, et je serai désolé qu’il crût à quelque intention malveillante. Il ne supposera pas, je l’espère, que je méconnais les services qu’il a rendus à la science. J’ai seulement cru plus utile d’insister sur les points où ses résultats me paraissent mériter d’être complétés, plutôt que sur ceux où je n’aurais pu que le répéter.” Poincaré’s objections to Duhem’s theory dealt with the entropy computation in a gaseous

agreed with Duhem on the increasing importance of the two Principles of Thermodynamics “in all fields of natural philosophy”, and on the rejection of “the ambitious theories full of molecular hypotheses”. Microscopic mechanical models could not account for the second Principle: in his words, “*mechanics collide with Clausius’ theorem*”. He claimed that he would have built up “the whole structure of mathematical Physics only on Thermodynamics”. The complexity of physical systems was not outside the intellectual horizon of Poincaré, for he had studied the stability of the three-body problem in celestial mechanics. He remarked that “the exact computation of the internal energy of a body depended on the state of external bodies”: the conservation of energy in a body called into play “the whole universe”. A similar remark had to be extended to the second Principle, although it was expressed “by an inequality” rather than an equality. He found that only following “the historical pathway” a scholar could understand why “all physicists adopted the two principles”. Poincaré shared with Duhem the sensitivity to the historical nature of the scientific enterprise, and the ability to perform both logical and historical analyses. Moreover, he was aware of the role of “metaphysical” or meta-theoretical issues besides purely “theoretical” ones.<sup>11</sup>

Poincaré’s Thermodynamics ranged from gases, fluids in motion, solids, and saturated vapours to sudden stresses in elastic bodies. He was interested in discussing the complexity of the real world, wherein “the pressure  $p$  does not have the same value in every point” or “the temperature  $T$  is not uniform, and the integral in Clausius’ theorem loses its definite meaning”. He put forward a “general demonstration of Clausius’ theorem” when some kind of irreversibility took place, either stemming from “heat exchanges with the sources” or from “the system itself”. Although he found no difficulties in reducing “the principle of equivalence to the fundamental principles of mechanics”, he found that “things are different” for the second Principle. He concluded that “irreversible phenomena and Clausius’ theorem cannot be explained by Lagrange equations”.<sup>12</sup>

Duhem’s appraisal of Poincaré’s treatise on Thermodynamics was very kind and very sharp at the same time. Poincaré’s approach to Thermodynamics appeared too abstract to Duhem, and he found Poincaré’s book “strange” mainly for this reason. However, the conclusions of the short review are quite balanced. He recommended students and engineers not to read the book, because they needed “clear and definite notions” on the subject, and they could be misled by a sophisticated approach. On the contrary, he heartily recommended the book to scholars who knew Thermodynamics, and were willing to “constantly subject their ideas to the riddle of criticism and contradiction”. Although the insights of “one of the most powerful and original minds of the time” could “often surprise” the readers, and sometimes shock them, Duhem was definitely convinced that scholars who “know Thermodynamics” would have found “Poincaré’s lessons” helpful.<sup>13</sup>

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mixture, and the interpretation of the Peltier effect: in particular, Poincaré criticised Duhem rejection of Maxwell’s conception of every electric current as a closed current. See *Ibidem*, pp. 321-38, 366-83, and 390.

<sup>11</sup> Poincaré H. 1892, pp. V, XII-XIV, and XVIII.

<sup>12</sup> See Poincaré H. 1892, pp. 98, 100, 103, 211-2, 392, and 422. He made extensive use of “Massieu characteristic functions”.

<sup>13</sup> Duhem P. 1892d, pp. 604-6. At first he remarked that Poincaré “was not a physicist by profession”, even though he found that Poincaré had seriously taken into account mathematical physics, and had offered the reader a critical analysis of the different theories put forward over time. Duhem looked upon Poincaré’s book as the result “of the impressions received by a powerful mind accustomed to cogitations of a different kind when undertaking a swift trip through physics”. Curiously enough, he compared Poincaré to a foreign scholar, in particular a Hindu



The following year Duhem published the second part of his *Commentaire*. As in the first part in 1892, the first chapter was devoted to some preliminary definitions and remarks. He faced the apparently inconsistent concept of “transformations which consist of a series of states of equilibrium”. He tried to give it “a logical meaning”, by resorting to the difference between geometrical parameters and state parameters. A physical system could experience a transformation without any change in its shape and position: under this condition, the transformation could be looked upon as a series of states of equilibrium.<sup>14</sup>

In reality, the whole 1893 *Commentaire* consists of a network of preliminary specifications and detailed remarks on heat, entropy, and the second Principle of Thermodynamics. There were “infinite reversible transformations” leading a physical system from a state  $(\alpha, \beta, \dots, \lambda, \text{ and } \vartheta)$  to a new state  $(\alpha', \beta', \dots, \lambda', \text{ and } \vartheta')$ , but for every reversible transformation, the integral  $\int dQ/F(\vartheta)$  had the same value: in the case of reversible cycles, it vanished. The specific case of ordinary mechanics was looked upon by Duhem as particularly important, for it was a specific application of his generalized Mechanics/Thermodynamics. Once again, when  $R_\alpha = R_\beta = \dots = R_\lambda = 0$ , automatically  $dQ = 0$ , and equations of “classical rational Mechanics” followed, where no reference to heat or temperature was made.<sup>15</sup> The fact is that, in this case, the concept of entropy and the second Principle lost their original meaning: if the mathematical derivation of Mechanics from Thermodynamics could be successfully performed, the conceptual relationship between them was still an open question.

It is worth mentioning that, in the same year, Poincaré published some notes on that conceptual relationship. In a short paper sent to a philosophical journal which had just started to be published, *Revue de Métaphysique et de Morale*, he compared the foundations of Mechanics and Thermodynamics. He found that “the mechanical conception of the universe” assumed two “different forms”: the mechanics of shocks and the mechanics of forces. In the first case, physicists imagined “atoms moving along a right line, because of their inertia”: the amount and direction of their velocity could not change unless “two atoms collide”. In the second case, atoms were imagined as submitted to a mutual “attraction (or repulsion), depending on their distance, and according to some law”. Since he saw the first conception as a “particular case of the second”, he was to disregard the distinction in the course of the paper. Moreover, he was to confine himself to discuss the “hindrances faced by the mechanists” and “experimental data”.<sup>16</sup>

According to Poincaré, Mechanics required that all phenomena were “reversible” with regard to time, because “reversibility” was “a necessary consequence of every mechanical hypothesis”. The fact is that ordinary experiences contrasted that requirement: thermal conduction was a well-known instance of irreversibility. That “a cold body gives back the heat it has received”, had never been observed. In this specific case, neither “direct

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Brahman, who tried to understand “our old Europe” looking through the windows of steamers or fast trains “during a swift tour”.

<sup>14</sup> Duhem 1893a, pp. 302-7. Duhem stated that “the concept of reversible transformation”, was one of “the most important and, at the same time, most problematic to be defined in Thermodynamics”. He summarized his view by assuming a “fundamental hypothesis”: “Il existe des systèmes pour lesquels toute modification, réelle ou virtuelle, qui est une suite continue d'états d'équilibre, est une modification réversible”. On the different meaning of the adjective “reversible” in W. Thomson, Clausius and other scholars, in particular on the difference between “irreversibility” and “irrecoverability”, see Uffink J. 2001, pp. 315-9.

<sup>15</sup> Duhem 1893a, pp. 337, 345, 355, and 357-8.

<sup>16</sup> Poincaré H. 1893, p. 534.

reversibility” nor “indirect reversibility” could take place after a physical system had passed “from a state  $A$  to a state  $B$  through a given path”. In other words, the system could go back from  $B$  to  $A$  “neither through the same path, nor through a different path”. The attempts to overcome this contradiction appeared “not sufficient” to Poincaré, Helmholtz’s hypothesis of “hidden motions” included.<sup>17</sup>

The recent developments of Mechanics, due to Poincaré himself, had shown that “a closed system submitted to the laws of mechanics” could repeatedly be found “near its initial state” over time. On the contrary, according to some cosmological interpretations of the second Principle of Thermodynamics, the whole universe would drift towards “a given final state, from where it will never come back”. If a radical thermodynamic world view envisioned a sort of thermal death, wherein “all bodies will be found at rest at the same temperature”, according to a radical mechanical world-view, we would be able to see “a flow of heat from a cold body to a warm one”, provided that we have “a little patience”. That Maxwell could expect thermal irreversibility to stem from the laws of Mechanics, seemed to Poincaré definitely inconsistent: no logical procedure could lead us to set up a deduction wherein “we find reversibility at the outset, and irreversibility at the end”.<sup>18</sup>

In 1894, in the third part of the *Commentaire*, Duhem returned to his 1891 “general equations of Thermodynamics”, unfortunate typographical ambiguities included. In the first chapter, he started from a physical system defined by the set of parameters  $\alpha, \beta, \dots, \lambda$  and  $\vartheta$ , which seemed a step backward with regard to the more general choice of parameters  $\alpha, \beta, \dots, \lambda, a, b, \dots, l$  he had introduced in 1892. Nevertheless, soon afterwards, he tried another kind of generalization: he took into account a “complex system” consisting of two “different and independent components”, whose internal energy, entropy, and thermodynamic potential were respectively

$$\begin{aligned} & Y_1(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1), \quad \Sigma_1(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1), \quad \mathcal{F}_1(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1) \\ & Y_2(\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2), \quad \Sigma_2(\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2), \quad \mathcal{F}_2(\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2) \end{aligned}$$

As in Duhem’s 1892 approach, the internal energy  $U = Y_1 + Y_2 + X_{1/2}$  of the complex system involved an interaction term  $X_{1/2}$ . Then he undertook a step forward, and considered “external bodies” or some kind of *environment*. The global internal energy  $\mathcal{U} = U + U' + \Psi$  had another kind of interaction term  $\Psi$ , apart from the internal energy  $U'$  of the environment.<sup>19</sup>

<sup>17</sup> Poincaré H. 1893, pp. 534-5.

<sup>18</sup> Poincaré H. 1893, pp. 536-7. In 1891 Poincaré had published a synthetic account of his mathematical theory on “the problem of three bodies” in the French *Bulletin Astronomique*. The classical problem had dealt with three masses  $A, B,$  and  $C$  “moving through a given plane”, where  $A$  was “a very great mass”,  $B$  a “very small” one, and  $C$  a negligible mass which could not influence the first two. Some solutions of the equations of motion were labelled “asymptotical” by Poincaré, because they led to “spiral orbits” which approached “asymptotically a closed curve” over time. As a consequence, the three bodies could be found “arbitrarily close to their initial positions”, and this could occur “an infinite number of times”. See Poincaré H. 1891, pp. 480, 487, and 490.

<sup>19</sup> Duhem 1894a, pp. 208-11. The new term  $X_{1/2}$  corresponded to the old term  $\Psi$  Duhem had introduced in 1892. The old term was now reserved to express the interaction of the complex system with the external world. This symbolic mismatch is quite puzzling indeed.

After having discussed the conditions of equilibrium for such a complex system, Duhem returned to the more general set of parameters  $\alpha, \beta, \dots, \lambda, a, b, \dots, l$  he had introduced in 1892, in the first part of the *Commentaire*. The first passage of the second chapter astonishes the reader 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.

Nous prenons, dans ce Chapitre, le mot *mouvement* pour désigner non seulement un changement de position dans l’espace, mais encore un changement d’état quelconque, lors même qu’il ne serait accompagné d’aucun déplacement. Ainsi, il y aurait mouvement si les variables que nous avons désignées par  $a, b, \dots, l$  ... variaient seules, les variables  $\alpha, \beta, \dots, \lambda$  gardant des valeurs fixes. De la sorte, le mot *mouvement* s’oppose non pas au mot *repos*, mais au mot *équilibre*.<sup>20</sup>

Then he opened another pathway: instead of starting from general equations, and then imposing the conditions for equilibrium, he started from the equations in the case of equilibrium, and tried to generalize them to the case of non-equilibrium, by means of new functions  $f_\alpha, f_\beta, \dots, f_\lambda$ :

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

The new functions represented “passive resistances to be overcome by the system”. Those resistances depended on basic parameters  $\alpha, \beta, \dots, \lambda, \vartheta$ , their time derivatives  $\alpha', \beta', \dots, \lambda'$ , and time  $t$ : from the mathematical point of view, they were “resistances” in the usual mechanical sense. Equilibrium was *perturbed* by actions which were the generalisation of mechanical *friction*: the total work  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$  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.<sup>21</sup>

Unfortunately the last  $n$  equations depended on the  $n+1$  Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ , and Duhem did not have at his disposal a mechanical generalization for the equation corresponding to the parameter  $\vartheta$ .

Lorsque l’état des corps extérieurs est donné à chaque instant  $t$ , les résistances passives deviennent des fonctions des variables

$$\alpha, \beta, \dots, \lambda, \vartheta, \alpha', \beta', \dots, \lambda', t.$$

<sup>20</sup> Duhem 1894a, p. 222.

<sup>21</sup> Duhem 1894a, pp. 223-4. In this case the symbolic mismatch seems even more puzzling: in 1891 Duhem had made use of the functions  $f_\alpha, f_\beta, \dots, f_\lambda$  in order to express explicitly the dependence of external forces on the basic parameters, namely  $A = f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta)$  and so on. In 1894, the new *dissipative forces*  $f_\alpha, f_\beta, \dots, f_\lambda$  had to be added to the already existing forces  $A', B', \dots, L'$ .

Les équations (2) deviennent lors des équations différentielles du second ordre, qui détermineraient les valeurs des variables  $\alpha, \beta, \dots, \lambda, \vartheta$ , en fonction de  $t$ , et, partant, le mouvement du système, si elles étaient en nombre suffisant ; *mais le nombre des variables dont il faut déterminer la valeur à chaque instant excède d'une unité le nombre des équations du mouvement fournies par la Thermodynamique* ; il faudra donc, pour compléter la mise en équations du problème, emprunter une dernière équation à une théorie physique étrangère à la Thermodynamique ; telle serait, par exemple, l'équation

$$\vartheta = \varphi(t)$$

qui ferait connaître à chaque instant la température du système.<sup>22</sup>

Duhem 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 tried to widen the scope 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:

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

In the  $\vartheta$ -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.<sup>23</sup>

Consistently with the conceptual framework of a generalized Mechanics, he put forward a “fundamental hypothesis” on the passive *resistances*  $f_\alpha, f_\beta, \dots, f_\lambda$ : 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

$$dS = \frac{dQ}{F(\vartheta)} = \frac{-[R'_\alpha \cdot \delta\alpha + R'_\beta \cdot \delta\beta + \dots R'_\lambda \cdot \delta\lambda + R'_\vartheta \cdot \delta\vartheta]}{F(\vartheta)},$$

in 1894

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

<sup>22</sup> Duhem 1894a, pp. 224-5.

<sup>23</sup> Duhem 1894a, pp. 225-6.

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

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

If  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda \leq 0$ , then  $\int \frac{dQ}{F(\vartheta)} \geq 0$ .

Duhem could finally identify the work  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$  with Clausius’ “uncompensated work”.

Clausius a donné à la quantité  $-(f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda)$ , qui est égale au travail des résistances passives changées de signe, et qui, par conséquent, n’est négative dans aucune modification réelle du système, le nom de travail non compensé accompli durant cette modification. La quantité  $EF(\vartheta)dS$  est au contraire, pour lui, le travail compensé accompli durant cette même modification.<sup>24</sup>

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

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

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”.<sup>25</sup>

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

<sup>24</sup> Duhem 1894a, pp. 228-9.

<sup>25</sup> Duhem 1894a, p. 229.

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”. According to Duhem, the latter had attained more success.<sup>26</sup>

He claimed that he had undertaken a third pathway: Thermodynamics as a wide-scope theory of transformations.

Nous avons essayé, dans le présent travail, d’indiquer une troisième position de la Dynamique par rapport à la Thermodynamique ; nous avons fait de la Dynamique un cas particulier de la Thermodynamique, ou plutôt, nous avons constitué sous le nom de Thermodynamique, une science qui embrasse dans des principes communs tous les changements d’état des corps, aussi bien les changement de lieu que les changements de qualités physiques.<sup>27</sup>

The “principles” of his “science” were based on the “experimental laws” established and “clarified” by Carnot, Mayer, Joule, Clausius, W. Thomson and Helmholtz. The mathematical framework had been outlined by Clausius and “improved” by Massieu, Gibbs and Helmholtz: they had shaped the “analytical features” of Thermodynamics. Duhem claimed that his theoretical and meta-theoretical design was in continuity with the recent tradition of physics rather than in competition with it. Nevertheless, at the meta-theoretical level, an interesting discontinuity appeared. 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.

Il nous semble qu’une conclusion générale se dégage de cette étude : si la science des mouvements cesse d’être, dans l’ordre logique, la première des Sciences physiques, pour devenir seulement un cas particulier d’une science plus générale embrassant dans ses formules toutes les modifications des corps, la tentation sera moindre, pensons-nous, de ramener l’étude de tous les phénomènes physiques à l’étude du mouvement ; on comprendra mieux que le changement de lieu dans l’espace n’est pas une modification plus simple que le changement de température ou de quelque autre qualité physique ; on fuira dès lors plus volontiers ce qui a été jusqu’ici le plus dangereux écueil de la Physique théorique, la recherche d’une explication mécanique de l’Univers.<sup>28</sup>

Only the distinction between the theoretical and the meta-theoretical level allows us to understand and appreciate 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 Duhem’s “more general science”.

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<sup>26</sup> Duhem 1894a, pp. 284-5.

<sup>27</sup> Duhem 1894a, p. 285.

<sup>28</sup> Duhem 1894a, p. 285.

## 5. Towards a General Theory of Transformations

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 essay had been written for the *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux*, and was printed by the Parisian publisher Hermann. It represented in some way the final stage of Duhem's theoretical, meta-theoretical and historical journey through the complex network of subject matters involving Physics and Chemistry. The *structural* analogy based on Analytical Mechanics, was exploited to its extreme consequences, and gave rise to very general equations.<sup>1</sup>

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 in his *Introduction à la mécanique chimique*. He briefly analysed the series of thermo-chemical 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”.<sup>2</sup>

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. The situation which chemists were facing around the middle of the century was thus summarized by Duhem:

*Lorsque les propositions de la thermodynamique classique font prévoir qu'un système sera en équilibre dans certaines conditions, il demeure, en effet, en équilibre lorsqu'on le place dans ces conditions ; mais il peut arriver qu'il demeure effectivement en équilibre dans les conditions où, selon la thermodynamique classique, il devrait subir certaines transformations.*

*Cette règle générale peut s'énoncer de la manière suivante :*

*Toutes les fois que la thermodynamique classique nous annonce l'impossibilité, pour un corps, de subir une certaine modification, la modification dont il s'agit ne peut, en effet, être réalisée expérimentalement ; mais lorsque la thermodynamique classique annonce qu'un corps passera*

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<sup>1</sup> At that time Duhem 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. See Brouzeng P. 1987, p. 163, and for more details, Jaki S.L. 1984, pp. 122-31.

<sup>2</sup> See P. Duhem 1896a, pp. 2-4. As in his 1893 book, 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.

*nécessairement d'un état à un autre, il arrive souvent que la modification annoncée ne se réalise pas.*<sup>3</sup>

Duhem aimed at “developing and completing thermodynamic theories” in order to account for both “true” and “false” equilibrium. The “hypothesis” which had excluded “false” equilibrium from his generalised thermodynamics appeared in his *Commentaire*. There he had stated that a system defined by its absolute temperature  $T$  and its “normal” Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ , is kept in equilibrium by “external actions”  $A, B, \dots, L$ , which “are specified, **without any ambiguity** in terms of  $\alpha, \beta, \dots, \lambda$  and  $T$ ”. When we invert the mathematical system, we find the set the set of values for parameters  $\alpha, \beta, \dots$ , and  $\lambda$  which correspond to “a state of equilibrium for the material system, when kept at the temperature  $T$ , and submitted to the external forces  $A, B, \dots, L$ ”:

$$\begin{aligned} A &= f_\alpha(\alpha, \beta, \dots, \lambda, T), & \alpha &= h_\alpha(A, B, \dots, L, T) \\ B &= f_\beta(\alpha, \beta, \dots, \lambda, T) & \beta &= h_\beta(A, B, \dots, L, T) \\ \dots & & \dots & \\ L &= f_\lambda(\alpha, \beta, \dots, \lambda, T), & \lambda &= h_\lambda(A, B, \dots, L, T) \end{aligned}$$

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”.<sup>4</sup>

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:

*Toutes les fois que la mécanique classique, où l'on fait abstraction du frottement, fait prévoir qu'un état du système étudié est un état d'équilibre, l'expérience confirme cette conclusion ; mais il peut arriver que le système soit en équilibre dans des états qui ne sont pas des états d'équilibre pour la mécanique des corps sans frottement.*<sup>5</sup>

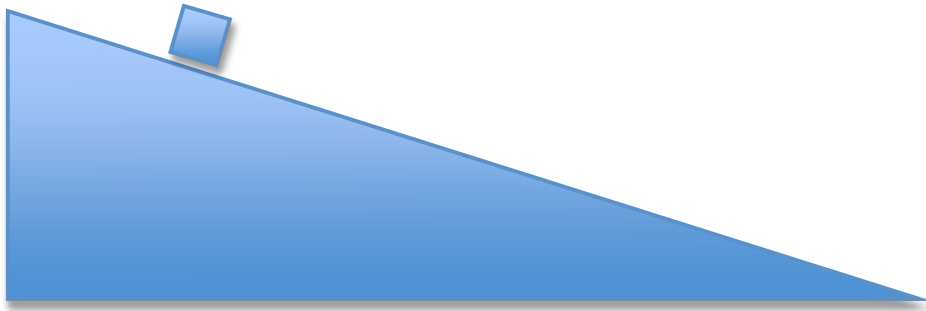
<sup>3</sup> Duhem P. 1896a, p. 5.

<sup>4</sup> Duhem P. 1896a, pp. 6-7. Duhem's choice of the bold font for the expression “without any ambiguity” is consistent with the importance he attributed to it. See in particular Duhem 1896a, p. 7: “... prenons, par exemple, à 200°C, un système qui renferme de la vapeur d'eau et les éléments de cette vapeur d'eau, oxygène et hydrogène, sous la pression invariable de l'atmosphère ; quelle que soit la fraction du système qui a passé à l'état de combinaison, quelle que soit celle qui est demeurée libre, le système est en équilibre ; nous pouvons donc, à la même température de 200°C, sous la même pression d'une atmosphère, observer une infinité d'états d'équilibre du système, et ces états d'équilibre forment une suite continue.”

<sup>5</sup> Duhem 1896a, p. 8.



The analogy appeared to Duhem not so astonishing as long as “the mechanics of bodies without friction is a specific instance of classic thermodynamics”. The existence of a limiting value in the plane inclination  $\alpha$  could be computed in terms of the forces applied to the body. The forces are: “the weight  $P$  of the body”, namely the *force* of gravity acting on it, “the pressure  $N$  of the body on the plane”, which is nothing else but the opposite of the normal component of  $P$ , and a *force* of friction  $F_a$ , which is imagined as a force acting upwards along the plane. This kind of force is commonly assumed to depend on  $N$  and on a coefficient  $f$ , which in its turn depends on the unspecified “nature of the body and the plane”. The translation of friction into a force is one of the commonplaces in Mechanics.



The specific expressions for the forces are:  $P = mg$ ,  $N = mg \cos \alpha$ , and  $F_a = fN = fmg \cos \alpha$ , where  $\alpha$  is the angle between the horizontal and the inclined plane. The forces acting along the plane are the horizontal component of gravity  $F = mg \sin \alpha$  and the *force* of friction  $F_a = fN = fmg \cos \alpha$ : they have opposite directions. Equilibrium is attained whenever the force of friction is greater than the horizontal component of gravity:

$$fmg \cos \alpha \geq mg \sin \alpha \quad \text{or} \quad \tan \alpha \leq f.^6$$

At that point, an important issue emerged from the core of mechanics: is friction a fundamental phenomenon or simply “a *fictitious* term”, which roughly synthesises the effects of “various and complex actions which explain friction” itself? In Duhem’s words, could “friction” be looked upon as a label attached to a set of “actions whose explicit and detailed analysis is impossible”? According to a “widespread opinion”, “natural bodies are more or less rough and pliable”; the disagreement would disappear only if we took into account that “roughness and pliability”. Duhem did not completely reject the “opinion” that some effects due to friction could really be removed by polishing the planes and choosing stiffer bodies. Nevertheless, some phenomena structurally similar to friction could not be reduced to a mere “appearance”, and could not be completely described by “classic mechanics”.<sup>7</sup>

<sup>6</sup> Duhem made two remarks: the condition of equilibrium is expressed by an inequality rather than an equality, and “the study of friction and the study of false equilibria show a very close analogy”. More specifically, the two fields of science, physics and chemistry, exhibited a formal analogy. See Duhem P. 1896a, p. 9: “*Les conditions d’équilibre d’un système à frottement s’expriment, non par des équations entre les forces agissantes et les variables, mais par des inégalités. Par conséquent, lorsque les forces agissantes sont données, l’état d’équilibre du système n’est pas déterminé ; mais on peut observer une infinité d’états d’équilibre formant un ensemble continu.*”

<sup>7</sup> Duhem P. 1896a, pp. 9-11.

He found it necessary to go beyond Gibbs' thermodynamics and even beyond his own previous beliefs: he honestly acknowledged that his "judgement" had changed "on this point". The "complex way of representation" he had put forward in 1893 called into play "very energetic actions, which were effective only at small distances". Those actions corresponded to a new term, an interaction term, which could be introduced in the thermodynamic potential. That conceptual and mathematical approach appeared now unsuitable for understanding false equilibrium, although it could account for phenomena like capillarity. It could also explain "why a bubble of steam cannot begin to grow inside a liquid", whereas "the liquid can vaporize where a bubble of steam or gas already pre-exists". His old theory could explain "*delays in boiling*", "*delays in condensation*", "*oversaturation in gaseous solutions*", and "*delays in decompositions*".<sup>8</sup>

According to Duhem, those phenomena could be classified as "seeming false equilibria". They were in accordance with "classic thermodynamics", provided that we did not confine ourselves to "a too simplified representation of bodies". Nevertheless, the complexity of some chemical processes challenged the *Energetics* which he had already set up. In order to tame that more demanding complexity, he preferred to *modify* the description of physical systems rather than the equations of the theory. He was aware that he was facing two "hypotheses", or meta-theoretical options, which could not be "disputed": both of them could lead to a consistent theory.

Si la réponse à cette question est affirmative, une contradiction entre les lois de la thermodynamique classique et l'expérience ne pourra jamais être qu'apparente ; elle pourra toujours se lever non point par l'introduction d'un terme complémentaire dans les équations fondamentales de la thermodynamique, mais par une plus grande complexité du système abstrait, reproduction schématique des corps sur lesquels on expérimente, auquel on applique ces équations.

Si, au contraire, on répond à cette question par la négative ; si l'on regarde l'établissement des lois de la mécanique et de la thermodynamique classique comme exigeant l'emploi de certaines hypothèses arbitraires, il ne sera nullement interdit de renoncer à ces hypothèses pour les remplacer par des suppositions plus compréhensives, de compléter les équations généralement admises par l'introduction de nouveaux termes et l'on pourra s'efforcer de rendre compte, au moyen de ces termes complémentaires, de classes de phénomènes jusqu'ici inexpliqués.<sup>9</sup>

Duhem had already undertaken the second way. He reminded the readers that, in the series of papers *Sur les déformations permanentes et l'hystérésis*, he had introduced "a new term in the equations of statics", in order to explain "permanent elastic strains", "magnetic hysteresis", and other phenomena wherein irreversible processes were involved. For the explanation of "friction and false equilibrium" he would have followed "a similar but distinct way": he would have further widened the structure of the equations of Analytical Mechanics. He found that the distinction between "actual viscosity" and "seeming viscosity", which he had put forward in the *Commentaire*, was still correct. In other words, there was a kind of viscosity which could be reduced to hidden mechanical effects, or "small local perturbations which we do not like to analyse in detail". But there was also an intrinsic viscosity, which

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<sup>8</sup> Duhem P. 1896a, pp. 12-13.

<sup>9</sup> Duhem P. 1896a, pp. 14-5.

could not be reduced to hidden mechanical effects: it corresponded to mathematical terms which had to “necessarily and essentially appear in the equations of motion” of a physical system.<sup>10</sup>

Duhem undertook two different generalisations. In the first, he took into account “a system independent of external bodies, with the same temperature in every point”, in some way an abstract system. The state of the system was defined by its temperature and a set of “normal parameters”  $\alpha, \beta, \dots, \lambda$ . In the mathematical-physical toolbox, Duhem put the living force  $\mathcal{T}$  of the system as a whole, the internal thermodynamic potential  $\mathcal{F}(\alpha, \beta, \dots, \lambda, T)$ , and the external forces  $A, B, \dots, L$ . To those basic functions he added the “passive resistances” or “viscous resistances”  $f_\alpha, f_\beta, \dots, f_\lambda$ , depending on the parameters  $\alpha, \beta, \dots, \lambda, T$  and their time derivatives  $\alpha' = \frac{d\alpha}{dt}, \beta' = \frac{d\beta}{dt}, \dots, \lambda' = \frac{d\lambda}{dt}$ . As Duhem remarked, the work done by the “resistances”

$$\left( f_\alpha \frac{d\alpha}{dt} + f_\beta \frac{d\beta}{dt} + \dots + f_\lambda \frac{d\lambda}{dt} \right) dt$$

could not be “but negative”. Generalized Lagrangian equations contained three kinds of terms: purely mechanical terms  $A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'}$ , classic thermodynamical  $\frac{\partial \mathcal{F}}{\partial \alpha}$ , and new viscous ones  $f_\alpha$ . The system was therefore described by the equations

$$A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} - \frac{\partial \mathcal{F}}{\partial \alpha} + f_\alpha = 0$$

.....

$$L + \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} - \frac{\partial \mathcal{F}}{\partial \lambda} + f_\lambda = 0.<sup>11</sup>$$

For this kind of system, wherein “all points have the same temperature”, and no influence was exerted by “external bodies”, the heat sent out in an infinitely small transformation was given by the expression

$$dQ = -\left( R_\alpha \cdot d\alpha + R_\beta \cdot d\beta + \dots R_\lambda \cdot d\lambda + C \cdot dT \right),$$

which had already been put forward by Duhem in 1891. The other 1891 relationship

<sup>10</sup> In the first chapter, Duhem briefly outlined the history of the interpretations of viscosity in the last decades. He put Navier, and subsequently Poisson, on the one side, and Stokes on the other. Navier had imagined a fluid as a collection of a huge number of “material points” submitted to “molecular forces”. Poisson had made use of molecular actions too, and had tried to “explain” viscosity and “rigidity of elastic solids”. Stokes, on the contrary, had confined himself to introducing “terms corresponding to viscosity in the equations of hydrodynamics”, and had not tried to explain “the origin of these terms”. See Duhem P. 1896a, pp. 15-19.

<sup>11</sup> Duhem P. 1896a, pp. 20-1.

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

had been updated in 1894:

$$\frac{dQ}{F(\vartheta)} = \frac{-[R'_\alpha \cdot \delta\alpha + \dots R'_\lambda \cdot \delta\lambda + C \cdot \delta\vartheta]}{E F(\vartheta)} = -dS - \frac{f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda}{E F(\vartheta)}.$$

It allowed Duhem to express the generalised thermal coefficients in terms of the entropy  $S$  and the functions  $f_\alpha, f_\beta, \dots, f_\lambda$ :

$$R_\alpha = T \frac{\partial S}{\partial \alpha} + \frac{f_\alpha}{E}.$$

.....

$$R_\lambda = T \frac{\partial S}{\partial \lambda} + \frac{f_\lambda}{E}.^{12}$$

The burden of irreversibility was loaded on the shoulder of the functions  $f_\alpha, f_\beta, \dots, f_\lambda$ . This mathematical way out allowed Duhem to transform  $dQ$  into the sum of two terms:

$$\begin{aligned} dQ &= -\left( T \frac{\partial S}{\partial \alpha} d\alpha + \frac{f_\alpha}{E} d\alpha + \dots + T \frac{\partial S}{\partial \lambda} d\lambda + \frac{f_\lambda}{E} d\lambda \right) = \\ &= -T dS - \frac{1}{E} \left( f_\alpha \frac{d\alpha}{dt} + f_\beta \frac{d\beta}{dt} + \dots + f_\lambda \frac{d\lambda}{dt} \right) dt. \end{aligned}$$

In the integration along a closed cycle of the expression  $dQ/T$  the term containing entropy vanished, and the integral reduced to

$$\int \frac{dQ}{T} = -\frac{1}{E} \int \frac{1}{T} \left( f_\alpha \frac{d\alpha}{dt} + f_\beta \frac{d\beta}{dt} + \dots + f_\lambda \frac{d\lambda}{dt} \right) dt.$$

Being negative the work done by dissipative forces  $f_\alpha, f_\beta, \dots, f_\lambda$ , the integral was positive, and it was consistent with ‘‘Clausius’ renowned inequality’’

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<sup>12</sup> Duhem P. 1896a, pp. 21-2. See also Duhem 1891, p. 234. In 1891 Duhem had started from a set of external forces  $A, B, L, \Theta$ . Afterwards, in the next sections of the paper, he confined himself to a simpler case, where the variation of  $\vartheta$  did not affect the other parameters, and  $\Theta = f_\vartheta = 0$ . Moreover he chose  $\vartheta = T$ .

$$\int \frac{dQ}{T} > 0.^{13}$$

In the second part of the book, Duhem introduced a purely mathematical transformation on the Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ :

$$\begin{aligned} \delta a &= \mu_{11} \delta \alpha + \mu_{12} \delta \beta + \dots + \mu_{1n} \delta \lambda \\ \delta b &= \mu_{21} \delta \alpha + \mu_{22} \delta \beta + \dots + \mu_{2n} \delta \lambda \\ &\dots \\ \delta l &= \mu_{n1} \delta \alpha + \mu_{n2} \delta \beta + \dots + \mu_{nn} \delta \lambda . \end{aligned}$$

At that stage, it was a very general linear transformation, devoid of any physical meaning. The forces  $A, B, \dots, L$ , the gradient of the potential  $\mathcal{F}$ , viscous forces, and the Lagrangian terms involving  $\mathcal{T}$  underwent the corresponding transformation, and were translated into more synthetic typographic symbols:

$$\begin{aligned} A, B, \dots, L &\rightarrow \mathcal{A}, \mathcal{B}, \dots, \mathcal{L} \\ \frac{\partial \mathcal{F}}{\partial \alpha}, \frac{\partial \mathcal{F}}{\partial \beta}, \dots, \frac{\partial \mathcal{F}}{\partial \lambda} &\rightarrow \Phi_a, \Phi_b, \dots, \Phi_l \\ f_\alpha, f_\beta, \dots, f_\lambda &\rightarrow \varphi_\alpha, \varphi_\beta, \dots, \varphi_\lambda \\ \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'}, \frac{\partial \mathcal{T}}{\partial \beta} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \beta'}, \dots, \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} &\rightarrow J_a, J_b, \dots, J_l . \end{aligned}$$

Therefore the equations of motion were formally expressed by the equations

$$\begin{aligned} \mathcal{A} - \Phi_a + J_a + \varphi_a &= 0 \\ \mathcal{B} - \Phi_b + J_b + \varphi_b &= 0 \\ &\dots \\ \mathcal{L} - \Phi_l + J_l + \varphi_l &= 0.^{14} \end{aligned}$$

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:

$$\mathcal{A} - \Phi_a + J_a + \varphi_a + g_a \frac{a'}{|a'|} = 0 .$$

<sup>13</sup> Duhem P. 1896a, p. 23.

<sup>14</sup> Duhem P. 1896a, pp. 67-8 and 70-2.

$$\mathcal{B} - \Phi_b + J_b + \varphi_b + g_b \frac{b'}{|b'|} = 0$$

.....

$$\mathcal{L} - \Phi_l + J_l + \varphi_l + g_l \frac{l'}{|l'|} = 0.$$

The new functions  $g_a, g_b, \dots, g_l$  were negative functions, and depended on the Lagrangian parameters  $a, b, \dots, l$ , their time-derivatives  $a', b', \dots, l'$ , and the forces  $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$ . Differently from the “viscous” forces  $\varphi_\alpha, \varphi_\beta, \dots, \varphi_\lambda$ , they did not vanish when the velocities vanished: on the contrary, they tended to the limiting functions  $\gamma_\alpha, \gamma_\beta, \dots, \gamma_\lambda$ , which depended only on  $a, b, \dots, l$  and  $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$ . 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”,

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

was negative.<sup>15</sup>

Only at this stage Duhem explained the physical meaning of the linear mathematical transformation on the Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ . The new set  $a, b, \dots, l$  could be split into two sub-sets: the parameters corresponding to the mechanical “motion” of the system as a whole, and the parameters corresponding to other generalised “motions”.

*Parmi les  $n$  quantités infiniment petites  $\delta a, \delta b, \dots, \delta l$ , données par les égalités (82), il en est six  $\delta m, \dots, \delta n$  qui jouissent de la propriété suivante : lorsque celles-là seules diffèrent de zéro, le système éprouve un déplacement d'ensemble dans l'espace, sans que ses diverses parties éprouvent ni changement d'état, ni changement de position relative ; celles des quantités  $g_a, g_b, \dots, g_l$  qui leur correspondent sont identiquement nulles.<sup>16</sup>*

As a consequence, 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”.

*Pour qu'un système entouré de corps extérieurs invariables, de même température que lui, et dont il est indépendant, soit in équilibre, il faut et il suffit que l'on ait les conditions*

<sup>15</sup> Duhem 1896a, pp. 72-5.

<sup>16</sup> Duhem 1896a, p. 74.

$$\left\{ \begin{array}{l} \gamma_a \leq \mathcal{A} - \Phi_a \leq -\gamma_a \\ \gamma_b \leq \mathcal{B} - \Phi_b \leq -\gamma_b \\ \dots\dots \\ \gamma_l \leq \mathcal{L} - \Phi_l \leq -\gamma_l \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} \mathcal{M} - \Phi_m = 0 \\ \dots\dots \\ \mathcal{N} - \Phi_n = 0 \end{array} \right. .^{17}$$

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

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

Si, avec Clausius, on donne le nom de *transformation totale* correspondant à la modification considérée, au quotient  $dQ/T$  ; le nom de *transformation compensée* à la quantité  $-dS$  ; enfin le nom de *transformation non compensée* à l’excès de la transformation totale sur la transformation compensée, on voit que l’on peut énoncer la proposition suivante :

*La transformation non compensée qui accompagne une modification réelle ne peut jamais être négative ; en général elle est positive.*<sup>18</sup>

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 1896 book, Duhem put forward specific applications; at the same time, he continued to bridge the gulf between Physics and Chemistry. For this purpose, the equations corresponding to  $\alpha, \beta, \dots, \lambda$  did not contain “inertial” terms:

$$\begin{aligned} \mathcal{A} - \Phi_a + \varphi_a + g_a \frac{a'}{|a'|} &= 0 \\ \mathcal{B} - \Phi_b + \varphi_b + g_b \frac{b'}{|b'|} &= 0 \\ \dots\dots & \\ \mathcal{L} - \Phi_l + \varphi_l + g_l \frac{l'}{|l'|} &= 0. \end{aligned} .^{19}$$

<sup>17</sup> Duhem P. 1896a, p. 77.

<sup>18</sup> Duhem 1896a, pp. 83-4. A misleading misprint appears in the equation above the quotation.

<sup>19</sup> Duhem P. 1896a, pp. 89-91. When we compare the set of equations (139) with the set (93), we notice the lack of the original Lagrangian terms  $J_k$  as a consequence of Duhem simplifications. See *Ibidem*, p. 90: “Enfin nous négligerons les variations de la force vive et, partant, les forces d’inertie.” This choice is quite problematic,

At this point Duhem called into play the thermodynamic potential  $H = \mathcal{F} + PV$ , which was a suitable potential for physical-chemical processes taking place at constant pressure. After having submitted  $\partial H/\partial\alpha$  and the other derivatives to the already mentioned linear transformation:

$$\frac{\partial H}{\partial\alpha}, \frac{\partial H}{\partial\beta}, \dots, \frac{\partial H}{\partial\lambda} \rightarrow \eta_a, \eta_b, \dots, \eta_l,$$

he showed the physical soundness of the typographic simplification

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

As a consequence, the generalised equations of motion assumed the more simplified structure

$$\begin{aligned} \eta_a - \varphi_a - g_a \frac{a'}{|a'|} &= 0 \\ &\dots \\ \eta_l - \varphi_l - g_l \frac{l'}{|l'|} &= 0. \end{aligned} \quad ^{20}$$

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. Duhem had added dissipative terms to Lagrange's 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. The last set of equations seemed to Duhem "very convenient" with regard to two points of view. On the one hand, they would have allowed him to "demonstrate statements which assume the existence of viscosity and friction" without any "detailed knowledge" of those effects, namely without having recourse to specific mechanical models. On the other hand, they could offer an invariant structure, "independent of" both the choice of the parameters and the specific expressions for  $\varphi_\alpha, \varphi_\beta, \dots, \varphi_\lambda$  and  $g_a, g_b, \dots, g_l$ . In the last

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because the new generalised mechanics could be looked upon as a replacement rather than a generalisation of the old one. The dramatic consequences will emerge in the next chapter of Duhem's book.

<sup>20</sup> Duhem P. 1896a, pp. 92-3. Duhem's potential  $H$  corresponded to Massieu's potential  $H'$  and Gibb's potential  $\xi$ .



section of the chapter, Duhem outlined a similar mathematical procedure for the set of Lagrangian parameters  $\alpha, \beta, \dots, \lambda, T, V$ , instead of  $\alpha, \beta, \dots, \lambda, T, P$ .<sup>21</sup>

However he confined himself to systems described by only one Lagrangian parameter  $\alpha$ , apart from “a uniform and constant pressure  $P$ ” and “a variable temperature  $T$ ”. Making use of non-transformed and transformed functions, Duhem wrote the *equation of motion* for this simple configuration:

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

When dissipative effects vanished, the equation became simply

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

It represented a curve in the plane  $(T, \alpha)$ , 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 already known inequalities

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

The boundaries of the “region of false equilibrium” in the plane  $(T, \alpha)$  corresponded to the equations

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) = 0 \quad \text{and} \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) = 0.^{22}$$

At this stage, some phenomenological remarks came into play, and Duhem translated them into a “hypothesis”. 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.

*HYPOTHESE - Lorsque la variation de la variable  $\alpha$  constitue un changement d'état chimique, les deux fonctions positives*

$$-\gamma(P, \alpha, T),$$

<sup>21</sup> Duhem P. 1896a, pp. 95 and 98. At the end, he emphasised once again how “convenient” the procedure was, and he found meaningful to add that he had made “a wide use of it in teaching at Bordeaux Faculty of Science”. See *Ibidem*, p. 98.

<sup>22</sup> Duhem P. 1896a, pp. 99-101.

$$-\Gamma(V, \alpha, T)$$

décroissent sans cesse lorsque la température croît ; elles ont de très grandes valeurs à basse température et tendent vers 0 lorsque la température s'élève.

Cette hypothèse peut s'énoncer de la manière suivante :

*Soit sous pression constante, soit sous volume constant, les deux lignes qui limitent la région des faux équilibres sont, à basse température, extrêmement éloignées de la ligne des équilibres véritables ; lorsque la température s'élève, elles se rapprochent de cette dernière ligne et tendent asymptotiquement vers elle lorsque la température croît au delà de toute limite.*<sup>23</sup>

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 concept of “friction” in Duhem’s generalized theory stemmed from a structural analogy between Mechanics and Chemistry. The word “friction” made sense in the context of Chemistry only after a re-interpretation of its original meaning. The behaviour of thermo-chemical processes with regard to temperature transformed the formal analogy into a more realistic analogy: 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.

On peut remarquer, d'ailleurs, que la dynamique, elle aussi, n'est parvenue à se constituer que du jour où les physiciens, et en particulier Galilée, ont osé faire abstraction du frottement et énoncer des lois dynamiques telles que la loi de l'inertie ; sans doute, la dynamique qu'ils ont ainsi créée est une dynamique trop simplifiée ; mais elle a frayé la voie à la dynamique plus complète où il est tenu compte du frottement.<sup>24</sup>

In the third chapter of the second part of his book, Duhem faced for the first time a specific chemical problem, with the help of phenomenological  $(T, \alpha)$  diagrams. He took into account a “compound together with the elements coming from its decomposition”: he labelled  $m$  the mass of the compound, and  $M$  “the greater mass of the compound consistent with the constitution of the system”. The Lagrangian parameter  $\alpha = m/M$  was a measure of the degree of combination of the chemical system. From the mathematical point of view,  $\alpha$  was a parameter changing with continuity between 0 and 1:  $\alpha = 0$  corresponded to the “complete dissociation”, and  $\alpha = 1$  to a combination “as complete as possible”. Duhem assumed, in

<sup>23</sup> Duhem P. 1896a, p. 104.

<sup>24</sup> Duhem P. 1896a, p. 105.

particular, that the chemical process was exothermic ( $R_\alpha < 0$ ) and took place at constant volume.

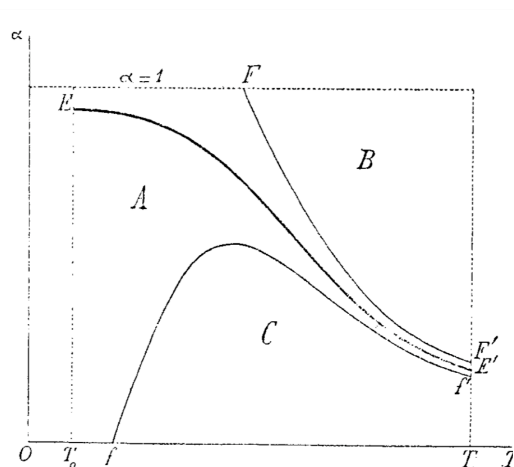


Figure 1 (Duhem P. 1896a, p. 106)

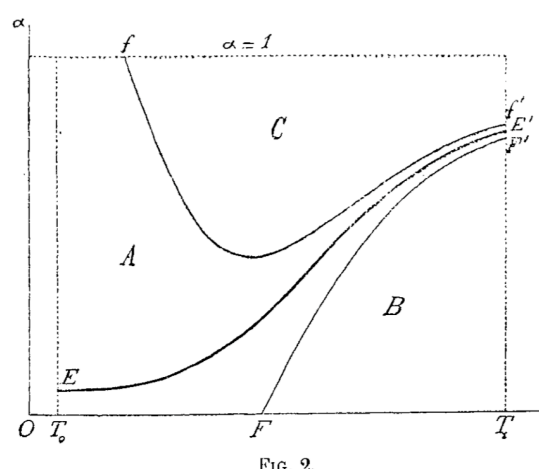


Figure 2 (Duhem P. 1896a, p. 107)

In Duhem's graphs for exothermic and endothermic processes,  $EE'$  was the curve of "true equilibrium", and  $FF'$  and  $ff'$  the curves describing the boundaries of the region  $A$  of "false equilibrium". The region  $B$  "was the seat of a dissociation", and the region  $C$  "the seat of a combination". For every given temperature, different initial states of the system led to different final states of equilibrium. The previous history of the physical system influenced the result of the transformation. The following passage made reference to exothermic processes.

Si l'on porte à une certaine température  $T$  un système qui, au début, ne renferme pas trace du composé, il s'y produira une combinaison jusqu'à ce que  $\alpha$  atteigne la valeur  $\alpha_1$ , ordonnée du point d'abscisse  $T$  sur la ligne  $ff'$ . Si, au contraire, on porte à la même température  $T$  un système qui, au début, ne contient que le composé, il s'y produira une dissociation, jusqu'à ce que  $\alpha$  soit réduit à la valeur  $\alpha_2$ , ordonnée du point d'abscisse  $T$  sur la ligne  $FF'$ . On a sûrement  $\alpha_2 > \alpha_1$ . Le système, maintenu à une température donnée, ne tend donc pas vers le même état limite, selon qu'il était au début à l'état de mélange ou à l'état de combinaison. C'est seulement à températures élevées que les deux limites sont sensiblement égales entre elles.<sup>25</sup>

The same kind of considerations were suitable for endothermic processes taking place at constant volume, as well as for both exothermic and endothermic processes taking place at constant pressure. Once again, Duhem pointed out that the exact shape of curves  $ff'$  and  $FF'$  could not be defined by his theory, but had to be derived from experiments.

The existence of states of "false" equilibrium corresponded to a sort of *laziness* of the system: it did not start its *motion* until the *friction* withholding the system was overwhelmed by the *forces* acting on it. The mechanical analogy put forward by Duhem in the first pages of the book suggested that, when a chemical compound was in the presence of its components,

<sup>25</sup> Duhem P. 1896a, pp. 106-7.

the mixture was in equilibrium until chemical *forces* became so strong as to trigger off a chemical reaction of combination or decomposition.

In accordance with his graphical representation (Picture 1 and Picture 2), Duhem imagined a chemical system “in a state of false equilibrium at a very low temperature”. When we “increase gradually” the temperature at constant volume or pressure, the “representative point” of the system describes a line which is “parallel to the axis  $OT$ ”. The system will remain in the region of false equilibrium until its representative line crosses the curve  $ff'$  or  $FF'$ . Duhem called  $\vartheta$  the temperature corresponding to this intersection: if we increase the temperature of the system beyond  $\vartheta$ , the system will undergo a combination or decomposition.

Nous pouvons donc énoncer les théorèmes suivants :

*Un système, pris avec une composition initiale donnée  $\alpha$ , est chauffé sous le volume constant  $V$  ; il n'éprouve aucune modification tant que la température est inférieure à une certaine valeur  $\vartheta(\alpha, V)$  ; lorsque la température surpasse la valeur  $\vartheta(\alpha, V)$ , il éprouve soit une combinaison soit une dissociation.*

*Un système, pris avec une composition initiale donnée  $\alpha$ , est chauffé sous le volume constant  $P$  ; il n'éprouve aucune modification tant que la température est inférieure à une certaine valeur  $\Theta(\alpha, P)$  ; lorsque la température surpasse la valeur  $\Theta(\alpha, P)$ , il éprouve soit une combinaison soit une dissociation.<sup>26</sup>*

The concept of false equilibrium was tightly linked to the concept of “point of reaction”. The temperature  $\vartheta(\alpha, V)$  was “the point of reaction under constant volume  $V$  of the system of composition  $\alpha$ ”, while  $\Theta(\alpha, P)$  was “the point of reaction under constant pressure  $P$ ”. The point of reaction depended obviously “on the initial composition  $\alpha$  of the system”, both at constant volume and pressure. Among the infinite points of reaction of the given system, Duhem stressed the importance of two of them: “*the point of combination*” corresponding to the initial value  $\alpha = 0$ , and “*the point of decomposition*” corresponding to  $\alpha = 1$ . The mixture of oxygen and hydrogen offered an easy instance of the point of combination. When heated either at constant volume or pressure, the two gases “remain blended” in a state of false equilibrium until a certain temperature was reached.<sup>27</sup>

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

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

<sup>26</sup> Duhem P. 1896a, p. 109.

<sup>27</sup> The points of reaction could be found at very different temperatures: for some mixtures, the point was placed at very high temperatures, and the chemical system “appears always to us in a state of false equilibrium”. According to Duhem, the mixture of hydrogen and nitrogen offered an instance of such behaviour. Other chemical reactions were very active at ordinary temperatures, since their point of reaction was placed at a very low temperature. Duhem briefly discussed “the mixture of frozen sulphuric acid and caustic soda, and the mixture of “sulphuric acid and potassium”. See Duhem P. 1896a, pp. 109-11.

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  $\alpha'$ , 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  $\alpha'$ . Then he assumed that the function  $\varphi(P, \alpha, T, \alpha')$ , which expressed the “viscosity” of the system, depended on  $\alpha'$  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

$$\begin{aligned} \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) - \Phi(P, \alpha, T) \cdot \alpha' &= 0, \\ \frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) - \Phi(P, \alpha, T) \cdot \alpha' &= 0. \end{aligned} \quad ^{28}$$

The simplified equations allowed Duhem to give a simple expression for the “velocity” of reaction in chemical processes, because  $\alpha'$  appeared only in the factorisation of the third term:

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

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  $ff'$  and  $FF'$  of the region of false equilibrium, wherein

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

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<sup>28</sup> Duhem P. 1896a, p. 128.

The denominator decreased when “viscosity” decreased, namely when the system approached classic thermodynamic behaviour.<sup>29</sup>

The structural analogy between Mechanics and Thermo-Chemistry required that an increasing *smoothness* in the first field corresponded to an increasing temperature in the second field. In other words, increasing temperatures *smoothed* dissipative effects. The simplification Duhem had introduced in this context was not structurally different from the hypothesis he had introduced in the previous chapter, provided that the function  $\Phi(P,\alpha,T)$  was a decreasing function of temperature.

L'expérience nous apprend que la valeur absolue de la vitesse d'une réaction donnée croit extrêmement lorsqu'on élève la température ; ainsi, selon M. Berthelot, la vitesse de transformation d'un alcool en éther par un acide est 22,000 fois plus grande à +200°C qu'au voisinage de +7°C : Ces résultats de l'expérience nous conduisent à énoncer l'HYPOTHESE suivante :

*La valeur absolue de la fonction  $\Phi(P,\alpha,T)$ , grande à basse température, devient extrêmement petite lorsque la température s'élève suffisamment.*<sup>30</sup>

The *structural* analogy between Mechanics and Chemistry led to “essential differences” between “the theory of motion of systems as taught by Dynamics”, and his new “theory on the modification of a system”. The difference dealt mainly with the role of “velocity”. In classic Dynamics, velocity was an initial information, to be given together with force, in order to solve differential equations involving accelerations. In Duhem's theory of false equilibrium, velocity was the outcome of a mathematical procedure starting from the knowledge of generalised forces.

Lorsque l'on considère un système dépendant d'une variable  $\alpha$  et dont la force vive varie avec  $\alpha$ , l'équation du mouvement du système a pour objet *immédiat* de déterminer  $d^2\alpha/dt^2$  lorsque l'on connaît non seulement l'état du système à l'instant  $t$  et l'action extérieure qui le sollicite à cet instant, *mais encore la valeur de  $d\alpha/dt$* , c'est à dire la vitesse des divers points du système à cet instant.

Au contraire, la théorie de la modification d'un système, lorsqu'on néglige les variations de force vive que ce système peut éprouver, nous montre que la vitesse de transformation  $d\alpha/dt$  est déterminée à un instant donné lorsqu'on ne connaît, à cet instant, l'état du système et l'action extérieure qui la sollicite. *La notion d'inertie ne s'étend pas à de semblables modifications.*<sup>31</sup>

Moreover, when the generalised viscosity vanished, velocity became infinite: this limiting case did not correspond to modern mechanics but to Aristotle's theory of motion. In order to better understand this theoretical result, Duhem compared this result with what happens in a pendulum, which undergoes free oscillations, and subsequently is progressively dampened. Starting from the free oscillations, we can imagine a gradually increasing viscosity acting on the pendulum, until it becomes critically dampened, and it approaches asymptotically the

<sup>29</sup> Duhem P. 1896a, pp. 129 and 131. There are some plus/minus misprints in Duhem's equations.

<sup>30</sup> Duhem 1896a, p. 131. Duhem's previous hypothesis on the behaviour of these systems relative to the temperature can be found on page 104.

<sup>31</sup> Duhem 1896a, p. 130.

position of equilibrium without any oscillation: an infinite velocity is excluded. In Duhem's simplified model of chemical transformations, the starting point was represented by a system strongly dampened: the velocity of the process increases with decreasing viscosity, until it becomes infinite when viscosity vanishes. We are facing two theoretical frameworks which cannot be transformed into each other.

If we try to reverse the process in Duhem's model, in order to set up a direct comparison with the mechanical motion of a pendulum, we should start from "motions" free from viscosity, namely a state with infinite velocity. When we increase viscosity, the velocity diminishes, but cannot vanish unless the system reaches the boundaries of the region of false equilibrium. This is what we can deduce from Duhem's mathematical model, at least in the simplified version expressed by the last equations. In those equations, velocity vanishes only when the numerator vanishes. On the contrary, when the numerator has a finite value, and the denominator vanishes, "velocity" becomes infinite: in this limiting case, in no way can the equations describe something similar to the traditional mechanical motion without dissipation.<sup>32</sup>

Duhem had looked upon his generalised physics as a generalisation of classic dynamics, which included systems undergoing dissipation, but now he realised that he had arrived at a sharp mathematical and conceptual gap between mechanics and chemistry. He realised that, starting from a *structural* analogy, he had reached a *structural* difference between classic dynamics and the application of his generalised physics to chemical reactions. The role of 'velocity' in Duhem's theory of dissipative systems was consistent with another *structural* analogy: Aristotle's theory of motion as a theory of material transformations. In the context of Aristotle's *physics*, it is not strange that, in the absence of some kind of resistance, velocity becomes 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 re-interpretation of Aristotle's natural philosophy. 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 ancient and modern science in a common mathematical framework: modern and ancient science appeared as different implementations of a very general formal structure.<sup>33</sup>

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. Moreover, the implicit but revolutionary re-interpretation of the history of science, which Duhem's theoretical researches were triggering off, collided with the contemporary mythology of scientific progress.

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<sup>32</sup> Duhem P. 1896a, pp. 130-1.

<sup>33</sup> 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. 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 M. 2004, pp. 8-13.

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.

The summary Duhem outlined in his “Conclusion” was, in some way, a plan for further researches. The first passages were devoted to “Clausius’ inequalities”: generalised viscosity and friction led naturally to those inequalities because of the corresponding negative work. Permanent elastic deformations, magnetic hysteresis, and quenching were other instances of phenomena described by mathematical laws consistent with “Clausius’ inequalities”. In other words, the second Principle of Thermodynamics stemmed from the negative work performed by dissipative actions and permanent deformations. What differentiated “the term of *viscosity*, the term of *friction*, and the term of *hysteresis*” from the other “terms already contained” in the equations was their behaviour with regard to time.

Under the transformation  $t \rightarrow -t$ , the first time-derivatives  $d\alpha/dt, \dots, d\lambda/dt$  transformed into  $-d\alpha/dt, \dots, -d\lambda/dt$ , whereas the second time-derivatives  $d^2\alpha/dt^2, \dots, d^2\lambda/dt^2$  remained invariant. Mechanical equations of the kind

$$A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} - \frac{\partial \mathcal{F}}{\partial \alpha} = 0$$

.....

$$L + \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} - \frac{\partial \mathcal{F}}{\partial \lambda} = 0$$

contained only quadratic terms in  $d\alpha/dt, \dots, d\lambda/dt$ , and therefore they were invariant under the transformation  $t \rightarrow -t$ , even though  $d\alpha/dt, \dots, d\lambda/dt$  were not. In brief, the equations of Mechanics were invariant under time-symmetry.

Il résulte de là que si un système peut éprouver une modification déterminée, ..., il peut également, sous l’influence des mêmes actions, parcourir *en ordre inverse* la même suite d’états, en ayant en chacun d’eux des vitesses égales en valeur absolue, mais contraires en signe, à celles qu’il possédait au moment où, dans la première modification, il a traversé le même état. Cette faculté laissée aux systèmes que régissent les seules équations de la thermodynamique classique, faculté que les oscillations d’une pendule nous manifestent sous la forme la plus simple, est celle que Helmholtz désigne comme la capacité d’éprouver des *modifications réversibles*.<sup>34</sup>

That invariance, or reversibility, did not occur in physical systems affected by “viscosity”, “friction” or “permanent transformations”. Duhem found that this deep difference represented an “insuperable hindrance” to reducing “complete thermodynamics ... to classic dynamics”. Two interpretations were at stake: either those mathematical terms described intrinsic features of the physical world, or they were fictitious terms which roughly described the effects of “*hidden motions*”. Duhem refused the second alternative; he had been “forced to

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<sup>34</sup> Duhem P. 1896a, p. 202.



acknowledge” that “the fundamental equations of dynamics” were “more complex than Lagrange’s equations”. He found that his point of view was consistent with Rankine’s *Energetics*. Two main issues deserved to be pointed out: the irreducible nature of dissipative effects, and the theoretical necessity of a general science of transformations.

La doctrine que le présent mémoire cherche à faire prévaloir est, en résumé, la résultante de deux idées fondamentales : la première est celle que nous trouvons déjà indiquée par Navier, dans un cas particulier : la viscosité et le frottement ne sont pas toujours des termes fictifs introduits dans les équations du mouvement des systèmes pour tenir compte sommairement de perturbations compliquées et mal connues ; ce sont souvent, dans ces équations, des termes essentiels, irréductibles et primitifs ; la seconde est celle que Rankine formulait dans son immortel écrit sur l’*Energétique* : les divers changements de propriétés d’un système ne se réduisent pas au mouvement local ; une même science doit réunir en ses principes à la fois les lois du mouvement local et les lois selon lesquelles se transforment les qualités des corps.<sup>35</sup>

In Duhem’s theory, Clausius’ inequality did not stem from “logical” or “experimental” reasons. It was the consequence of a specific hypothesis: the work done by “viscosity” or “friction” had been assumed to be negative. In this sense, Clausius’ inequality, namely the second Principle of Thermodynamics was not a physical necessity, but the consequence of an “arbitrary” hypothesis. He claimed that his theory would not have been overthrown by the opposite assumption of a “positive friction”. The hypothesis of the positive work done by *dissipative forces* echoed the creative power of life.

Lorsqu’on analyse les propriétés des systèmes où le travail de la viscosité et du frottement ne seraient plus essentiellement négatifs, où les transformations non compensées ne seraient plus essentiellement positives, il est impossible de ne pas être frappés des analogies que ces propriétés présentent avec celles des tissus vivants, soit animaux, soit végétaux ; de ne pas remarquer la facilité avec laquelle elles rendent compte de la plupart des synthèses organiques, inexplicables à la mécanique chimique ordinaire, irréalisables, hors de l’organisme, *dans les conditions de température où l’organisme fonctionne*.<sup>36</sup>

Life sciences suggested the possibility of a “new thermodynamics” or a “*physiological thermodynamics*”, which satisfied the Principle of the conservation of energy but would not satisfy “*the principle of the impossibility of perpetual motion*”. In the course of almost three centuries, many scientists had tried to reduce phenomena of life to mechanical actions. Duhem hinted at a complementary perspective: the study of phenomena occurring in living matter could help scientists to better understand physical and chemical phenomena of high complexity.

D’ailleurs une autre interprétation des synthèses organiques accomplies à l’inverse des prévisions de la thermodynamique semble susceptible de se substituer à la précédent. On n’a

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<sup>35</sup> Duhem P. 1896a, p. 205.

<sup>36</sup> Duhem P. 1896a, p. 206. Duhem replaced the expression “Clausius’ inequalities”, which appears in the first passages of Duhem’s “Conclusion”, with the corresponding singular expression “Clausius’ inequality” in the following passages.

d'exemples certains de semblables synthèses que celles que se produisent au sein du protoplasme chlorophyllien soumis à l'action de la lumière ; n'est-ce point cette dernière action qui doit être invoquée comme la cause du désaccord entre les faits et les prévisions de la thermodynamique ? Nous avons vu ... la lumière diminuer la valeur absolue des termes de viscosité et de frottement ; ne pourrait-elle aller jusqu'à changer le signe de ces termes ? Ne pourrait-elle produire, au sein du protoplasme chlorophyllien, des actions accompagnées d'un travail positif du frottement ou de la viscosité ? Ne pourrait-elle agir de même en dehors de l'organisme, ce qui expliquerait certaines actions photographiques?<sup>37</sup>

Duhem hinted at a possibility which was distant at that time: both the complexity of the physical world, and the creative power of life were outside the horizon of physics. Only after many decades, were some physicists and chemists to attempt to resume Duhem's heritage.

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<sup>37</sup> Duhem P. 1896a, p. 207.

## Concluding Remarks

Duhem continued to publish papers and books on theoretical physics until his death in 1916. In 1903, in his historical and critical analysis of the foundations of physics, he wondered how dissipative effects, irreversible in their nature, could be reduced to hidden microscopic reversible motions. Should scientists be satisfied with the explanation of “negative work” of dissipations, or “unbalanced transformations” which made entropy increase, in terms of mechanical actions? Why, in other words, did nature transform hidden microscopic motions only into negative work? Why, he asked himself, “among the endless variety of hidden and ordered motions”, were only those corresponding to “passive resistance” actually implemented by Nature? According to Duhem, Mechanics, as it was supposed to be, seemed “to have no answer” to the following question: why other kinds of motion “do not occur”?<sup>1</sup>

The relationship between Mechanics and Thermodynamics was the keystone of Duhem’s physics, and at the same time an important subject matter in his histories of physics. He thought that the statement “all physical phenomena can be mechanically explained” was neither true neither false “from the experimental point of view”: it was “*transcendente à la méthode physique*”. In order to decide the issue, scientists had to resort to the reasons of “Metaphysics”, or to pragmatic reasons involving “convenience”. The query underwent a psychological drift when Duhem mentioned “different mental attitudes with regard to physical theories”: there were “abstract” minds and “imaginative” minds. If the former did not suffer “because of the lack of mechanical explanations”, the latter could “not be satisfied” until some kind of geometrical representation was available. Duhem did not hide his distrust of “imaginative” physicists: were “hidden masses and motions” more acceptable than “*occult* forces of ancient Scholastic”? Moreover, if a mechanical model could be put forward “to explain a set of physical laws”, then many, if not infinite, other models could satisfy the same requirement. From the methodological point of view, making use of specific theoretical models appeared to Duhem as a constraint and a waste of intellectual energy: “every section of physics would require a specific model, which could not have any link with the model corresponding to the previous section”.<sup>2</sup>

In 1906 Duhem published the book which made him famous as a philosopher of science, *La théorie physique, son objet – sa structure*. In the book he collected and updated the content of some papers he had published in the 1890s, mainly in the Belgian *Revue des questions scientifiques*. I cannot analyse the book in detail here, but only remind the reader that, alongside an original re-evaluation of Aristotle and Pascal’s views on the knowledge of the natural world, he put forward subtle meta-theoretical remarks on aims and methods of physics. His point of view was re-shaped by other scholars in the second half of the twentieth century, but only recently Duhem has been properly understood and attentively quoted. He specified that his remarks were not “general ideas” on science, or abstract “cogitations in competition with concrete details”, but specific remarks which had emerged from *inside* his “daily practice of science”. From the branched structure of the book I would like to single out

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<sup>1</sup> See Duhem P. 1903, in Duhem P. 1992, p. 156: “La Thermodynamique impose à tous les phénomènes du monde matériel une tendance dans un même sens ; il n’en résulte pas que ces phénomènes ne puissent tous s’expliquer par des combinaisons de figures, de mouvements, de masses et de forces. Mais l’hypothèse que tous les effets de la matière brute sont d’essence mécanique ne rend aucun compte de la commune tendance qui sollicite tous ces effets.”

<sup>2</sup> See Duhem P. 1903, in Duhem P. 1992, pp. 184, 186-9, and 190-93.

only the concept of “*natural classification*”. Physical theories could not be “*explications*”, but simply mathematical deductions from few physical principles. At the same time, a physical theory was something more than a mere alliance between mathematical structures and empirical laws. There was also a conceptual scaffolding where “common sense and mathematical logic ... mix with each other in an inextricable way”, in order to catch “the real connections among things themselves”. The soundness of that conceptual network depended neither on empirical nor on formal procedures. It had to do with Pascal’s “*esprit de finesse*”: it was a meta-theoretical sensitivity which could help scientists overcome the essential tension between “dogmatism” and “scepticism”.<sup>3</sup>

In some passages of his book Duhem explicitly mentioned and quoted Pascal: in any case, Pascal represented a methodological landmark for him. In the last decades, scholars have pointed out that Duhem’s reference to Pascal was appreciated neither by “positivist atheists ... for whom science offered a paradigm of reliable knowledge”, nor by “scholastically minded Catholic apologists”. The latter “needed a reliable science to support their natural theology”, and feared that “scepticism about any branch of knowledge implied religious scepticism as well”.<sup>4</sup>

Duhem was conscious of the complex relationship between experimental and theoretical practices. On the one hand, a single “*empirical fact*” could be translated into “*an infinite number of different theoretical facts*”. On the other hand, without assuming the validity of some basic theories, no physical experiment could be performed and interpreted. Just for this reason, an experiment could not lead to the confutation of a single hypothesis or theory: the confutation had a global effect on the whole “theoretical scaffolding” which assured the intelligibility of the experiment. According to Duhem, a physical theory required a complex conceptual link between the domain of scattered facts and the domain of mathematical certainty: this awareness was a hallmark of late nineteenth-century theoretical physics.<sup>5</sup>

In 1911 he published the two-volumes *Traité d'énergétique ou de thermodynamique générale*, where he collected and updated most of his researches in theoretical physics. After having reminded the reader that the aim of theoretical physics was “connecting the existing laws with each other, in accordance with some *general principles*”, he stressed the importance of “*Rational Mechanics*” as the specific “code for the general principles of physics”. In other

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<sup>3</sup> Duhem P. 1906, pp. 1-2, 26, 36, 440-1, and 444. In 1998 John Heilbron reported a conversation with Kuhn, wherein the latter discussed a “vision” of science as a body of knowledge which “does not advance towards the truth, but from less to more powerful taxonomies of nature”. See Heilbron J. 1998, p. 513, footnotes 30 and 31 included. Once again, buried memories suddenly and unobtrusively flow through the history and philosophy of science. See footnote 1 in chapter 4.

<sup>4</sup> See Martin R.N.D. 1991, p. 68; see also Stoffel J-F. 2002, p. 196. In 1922 the French mathematician Émile Picard had claimed that Pascal was the most meaningful reference for Duhem’s theory of knowledge. He also stressed how important Pascal was for Duhem in the specific context of physics of continuous media. See Picard É. 1922, pp. CXXXV-CXXXVII, and CXXX. I find quite convincing Stoffel’s remark that Duhem and Pascal had in common a whole world-view, which was “at the same time scientific, philosophical and religious”. See Stoffel J-F. 2007, p. 293. Nevertheless I find potentially misleading Stoffel’s statement that “Duhem is neither Aristotelian, nor Thomist, ... but Pascalian”. For the same reason I cannot agree with Martin on his statement that “everything we know about Duhem ... points away from Aristotle and towards Pascal”. See Stoffel J-F. 2002, p. 345, and Martin R.N.D. 1991, p. 90. Pascal’s alleged *scepticism* was not so different from the awareness of the boundaries of rational knowledge as codified by Aristotle in his *Posterior Analytics*. When Martin stated that “Duhem has ... subjected physics to a perpetual tension between intuitive and deductive factors” (Martin R.N.D. 1991, p. 115), I find that the tension under consideration is nothing else but the tension on which Aristotle had tried to cast some light. Obviously, I also find that Aristotle’s *Posterior Analytics* had little in common with neo-Thomism.

<sup>5</sup> Duhem P. 1906, pp. 217, 274, 303, and 328.

words, Rational Mechanics offered the formal structure or the formal language for physics, even for the fields of physics which did not deal with mechanics. The language of rational mechanics had nothing to do with the specific mechanical models which had been used by some physicists in the context of Thermodynamics. That language had nothing to do with the “*mechanical explanation of the Universe*” which, according to Duhem, had completely failed. The arrangements of “geometrical models and local motions” had to be distinguished from “the rules of Rational Mechanics”. The generalisation of those rules or “the code of the general laws of physics” was nothing else but his rational thermodynamics or “*Energetics*”.<sup>6</sup>

Once again, on the track of his 1906 book, Duhem stressed the conceptual gap between the empirical and theoretical practice: a theory was not required to “take into account the facts of experience”, but only to take care of its internal consistency. Only at the end of a complex process, the results of mathematical procedures had to be compared with “experimental laws”. Nevertheless, a theory could not be designed “at random”: it required “a justification”, but that justification was “historical” rather than “logical”. The history of physics was a melting pot of experiences, hypotheses, mathematical tools, specific theoretical models, wide-scope conceptual streams, and meta-theoretical options, but also the stage-set where the emergence, development, and fall of physical theories had found their representation. History of physics had shown how “the different principles” had to be “modified” or “improved”, in order to reach “a partial and however imperfect confirmation”. History had taught us that those principles could never “fit exactly reality”: we had to “reject or retouch” them continuously, according to a dynamical process which could lead us to approach a natural classification.<sup>7</sup>

In 1911, the role of the history of science in Duhem’s intellectual enterprise had become more prominent. In 1905-06 he had published the two volumes of *Les origines de la statique*, and the first part of *Études sur Léonard de Vinci: ceux qu’il a lu et ceux qui l’ont lu*. The second part was published in 1909, and the third in 1913, while in 1908 ΣΟΖΕΙΝ ΤΑ ΦΑΙΝΟΜΕΝΑ, *Essai sur la notion de théorie physique de Platon à Galilée* had appeared. Starting from 1913 he published the first four volumes of his monumental *Le système du monde. Histoire des doctrines cosmologiques de Platon à Copernic*. Since then, he has been looked upon as an authoritative, even though controversial, historian of science, and his researches in theoretical physics have remained in the background.

Now we can ask ourselves what heritage Duhem left to twentieth-century science, in particular what remains now of his physical theories.<sup>8</sup> I am aware that the scientific fruitfulness can be found at different levels: at the level of specific theoretical models, the level of the general theoretical streams, or at the level of meta-theoretical commitments. In the tradition of theoretical physics, which had just emerged in the last decades of the nineteenth century, we can distinguish these different levels. The first level corresponds to the specific hypothesis and algorithms to be applied to phenomena under investigation. The

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<sup>6</sup> Duhem P. 1911, tome I, pp. 1-3.

<sup>7</sup> Duhem P. 1911, tome I, pp. 4-5.

<sup>8</sup> 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 A., and Deltete R.J. 2004, p. 223). See also Brouzeng P. 1981a, pp. 241-61.

second level corresponds to wider-scope principles and hypotheses, and to their interplay. Finally, the third level corresponds to the methods and aims of scientific enterprise. I would like to offer some instances. In the case of Duhem's 1896 essay, investigated in the last chapter of the present preview, the choice of specific phenomena (for instance "false chemical equilibrium"), the choice of new Lagrange-like equations, and the interpretation of "viscosity" and "friction" are first-level options. That mechanics, thermodynamics, and chemistry might be different implementations of a very general mathematical framework, or that the natural world had to be described by continuous models, are second-level options. As instances of Duhem's third-level options I mention the rejection of Galileo's reductionism, the commitment to describing the complexity of the physical world, and the stress on the intrinsic historicity of scientific enterprise.<sup>9</sup>

I find that something of Duhem's physics has survived, at different levels, although in an unexpected way. The majority of Duhem's specific theoretical models, and his specific mathematical approach have not survived, but some issues have survived, and have found new implementations. Among them, I list:

1. Physics and Chemistry can be unified by means of a powerful mathematical framework;
2. Classic Thermodynamics can emerge from a generalisation of Analytical Mechanics;
3. A new physics can describe the complexity of the real world.

Half a century after Duhem's death, the complexity of the physical world began to attract some physicists and chemists. The buried memory of his theoretical physics re-emerged and found new implementations. But that re-emergence was, in some way, a fresh start.<sup>10</sup>

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<sup>9</sup> This historiographical sketch suits the specific season of theoretical physics we are dealing with, and perhaps the decades going roughly from 1880s till 1920s: it cannot be extended upon a longer time span. See Bordoni S. 2008, pp. 264-6.

<sup>10</sup> On the subsequent debate on the new trend in physics after the second World War, and on the re-emergence of the interest in the complexity of the physical world, see Cocconi G. 1970, pp. 83 e 87, Anderson P.W. 1972, pp. 393 e 395, and Schweber S. 1997, pp. 659-71.

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