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Taming complexity

Duhem's third pathway to Thermodynamics

Editrice Montefeltro

Editrice Montefeltro s.r.l.
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URL: **www.editricemontefeltro.it**

Stampato per i tipi della Editrice Montefeltro s.r.l. nel mese di Ottobre 2012

Codice ISBN: 978 88 85363 58 8

To Lorenzo, Giovanni, and Francesco,
who have taught me the waywardness of history.

Acknowledgements

I should like to thank Enrico Giannetto for having introduced me to Pierre Duhem's theoretical physics, and Salvo D'Agostino and Enrico Giannetto for their general comments on the manuscript. My thanks also to Paolo Campogalliani for his specific remarks on the early history of thermodynamics, Sandro Caparrini for useful specifications on twentieth-century thermodynamics, and Jean-François Stoffel for an interesting exchange on Duhem's philosophy. And finally, I should like to thank Mario Alai, Vincenzo Fano and Gino Tarozzi, for having provided every kind of support throughout the last stage of my research.

It gives me great pleasure to thank the Max-Planck-Institut für Wissenschaftsgeschichte, and in particular Jürgen Renn, for having given me the opportunity to present and discuss the content of the present book. I also thank Massimiliano Badino for the interesting and helpful confrontation on the foundations of 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.”
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> (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 book 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.[1]

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[1] 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"

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".[2]

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 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

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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.

[2] 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."

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.[3] 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.[4]

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

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[3] 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.

[4] 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.

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.[5]

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.[6]

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 histori-

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[5] 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.

[6] 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."

cal 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.[7] 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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[7] 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.[8] 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 thermo-

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[8] 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.”

dynamics. 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.[9]

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 sort of contrivance but the suitable intellectual tool to describe the evolution of a great population of molecules.[10]

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.[11]

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[9] See chapter 1 in the present book. 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.

[10] See chapter 2 in the present book. 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.

[11] See chapter 3 in the present book. 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. Se also Brush S. 1976, book 1, pp. 96 and 239, and Brush S. 1976, book 2, pp. 356-63.

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".[12]

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.[13]

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 general-

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[12] See chapter 4 in the present book. 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.

[13] See chapter 5 in the present book.

ized 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 developed : ordinary mechanics had already become "a particular case of a more general science".[14]

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 began 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.[15]

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.[16]

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[14] See chapters 6 and 7 in the present book. See also Duhem P. 1886, pp. 11-13, and Duhem P. 1894a, p. 285.

[15] See chapters 8, 9, and 10 in the present book. See also Duhem P. 1896, p. 205.

[16] 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."

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.[17]

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 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.[18]

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 phi-

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[17] 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 ; … »

[18] See Duhem P. 1903, in Duhem P. 1992, pp. 199 and 218-9.

losophers 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.[19]

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

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[19] 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 McCormmach 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.

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

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.[21]

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

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[20] It is worth mentioning that, in 1898, the mathematical physicist Georg Helm classified Clauisus as "an out standing representative of theoretical physics" ("ein hervorragender Vertreter theoretischer Physik"). See Helm G. 2000, p. 383 (Helm G. 1898, p. 343).

[21] 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.

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.[22]

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

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

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[22] Kuhn T.S. 1976, pp. 5 and 8.

[23] 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.

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.[24]

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.[25]

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 explana-

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[24] 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.

[25] 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."

tions. 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 metatheoretical options we find Hertz and then Planck: they followed Rankine, Maxwell, Clausius and Helmholtz's similar attitude. The debates involved Helm against Planck, and FitzGerald against Ostwald.[26] 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 achieve-

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[26] 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 McCormmach 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.

ments. Science had finally managed to realize, at least in part, Bacon's dream, and the myth of scientific progress emerged.[27]

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.[28]

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. As a consequence, a great expectation also emerged: scientific progress could trigger off a more general social progress.[29]

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

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[27] 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.

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

[29] 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.

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.[30]

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"?[31] 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*.[32]

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[30] 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.)

[31] I am referring to the title of Feyerabend's famous essay (Feyerabend P.K. 1970).

[32] 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,

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 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.[33]

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.[34]

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.

[33] 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.

[34] 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 –

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.[35]

Duhem had kept together what subsequently scholars split into two different subject matters, namely history and philosophy of science.[36] Even though the present book 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. If 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 between "phenomenism" and "phenomenalism", concluded that "he

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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."

[35] 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.

[36] 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".

was realist in his heart, but phenomenalist in his mind". In 2011, Paul Needham credited Duhem with "moderate realism".[37] 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".[38]

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 con-

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[37] 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.

[38] 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)

tents into apologetic arguments, and always insisted on “a sharp separation between science and faith”.[39]

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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[39] 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. DIFFERENT HISTORICAL FRAMEWORKS 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".[1]

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.[2]

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[1] Bryan G.H. 1891, pp. 85 and 121.

[2] 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

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.[3]

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 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".[4]

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universe" when associated to "the kinetic theory of gases, as developed by Maxwell and Boltzmann". (Magie W.F. 1899, p. vi)

[3] 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.

[4] 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.

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".[5]

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.[6]

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

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[5] Clausius R. 1850, in Clausius R. 1864, pp. 17-8.

[6] 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.

power of heat", although "founded on an axiom contrary to his fundamental axiom" on "the permanence of heat".[7]

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 thermo-dynamic 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 different form, and was then unknown to Thomson himself.[8] 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.*[9]

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 thermo-dynamic 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".[10]

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[7] Thomson W. 1851, in Thomson W. 1882, pp. 174-7 and 185.

[8] Thomson W. 1851, in Thomson W. 1882, pp. 180-3, the footnote at pp. 182-3 included.

[9] Thomson W. 1851, in Thomson W. 1882, p. 179.

[10] Thomson W. 1852, in Thomson W. 1882, p. 511.

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.[11]

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, …
> 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.[12]

In 1854, once again Clausius stated that the equivalence between heat and work, and "Carnot's proposition" did not necessarily clash,

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[11] 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.

[12] Thomson W. 1852, in Thomson W. 1882, p. 514.

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 schliesslig 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.*[13]

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 formulation of the second principle.[14] 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.

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[13] Clausius R. 1854, in Clausius R. 1864, p. 133. See also pp. 127-8.

[14] 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)

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".

> 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.[15]

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 $K_1, K_2, ..., K_n$ bodies, to be found at the temperatures $t_1, t_2, ..., t_n$, he assumed that the quantities $Q_1, Q_2, ..., Q_n$ 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

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

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[15] Clausius R. 1854, in Clausius R. 1864, p. 143.

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.[16]

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*.
> Es wurde bei dem Beweise des Satzes, dass in einem beliebig zusammengesetzen 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.[17]

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,

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[16] Clausius R. 1854, in Clausius R. 1864, pp. 140, 144-5, and 147.

[17] Clausius R. 1854, in Clausius R. 1864, pp. 151-2.

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".[18]

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.
> 3) Der Einfluss der Molecularkräfte muss verschwindend klein seyn.[19]

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[18] Clausius R. 1854, in Clausius R. 1864, p. 152.

[19] 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

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 sämmtlichen 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 fasten 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.[20]

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.[21]

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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 crée l’innovation …”

[20] Clausius R. 1857, in Clausius R. 1867, pp. 235-6.

[21] Thomson W. 1862, in Thomson W. 1889, p. 349.

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 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".[22]

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

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

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[22] 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.

where the equality made reference to "cycles taking place in a reversible way", and the inequality to "irreversible transformations".[23]

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 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.[24]

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 mean-

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[23] Clausius R. 1865, in Clausius R. 1867, pp. 1 and 3.

[24] 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.

ings 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".[25]

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.[26]

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 "Verwand-

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[25] Clausius R. 1865, in Clausius R. 1867, pp. 34-5.

[26] Clausius R. 1865, in Clausius R. 1867, p. 44.

lungsinhalt" and "Disgregation" faded into the background. Clausius' 1854 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 Clauisus' 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".[27]

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.

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[27] Duhem P. 1893e, pp. 138-9.

> 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[28]

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*.[29]

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".[30]

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

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[28] Duhem P. 1895c, in Duhem P. 1992, p. 399.

[29] Duhem P. 1895c, in Duhem P. 1992, pp. 401 and 411.

[30] Duhem P. 1895c, in Duhem P. 1992, pp. 419 and 422.

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".[31]

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.[32]

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

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[31] Duhem P. 1895c, in Duhem P. 1992, pp. 436-9.

[32] Duhem P. 1903, in Duhem P. 1992, p. 110.

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 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.[33]

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".[34]

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

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[33] 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."

[34] See Duhem P. 1903, in Duhem P. 1992, pp. 141-3.

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 19th-century work in the kinetic theory of gases".[35]

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 they could be reformulated in a way that did not depend on the assumption of a conserved heat substance".[36]

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".[37]

After a few years, the mathematical physicist and historian of physics Clifford A. Truesdell inquired into the relationship between the

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[35] 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.

[36] 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.

[37] Brush S.G. 2003a, in Brush S.G. (Hall N.S. ed.) 2003, p. 484.

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".[38]

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

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[38] 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."

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".[39]

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".[40]

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.[41]

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,

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[39] 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 CLAUSIUS" had frequently been "repeated, embroidered, and glossed in all the textbooks", even though their 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.

[40] See Duhem P. 1895c, in Duhem P. 1992, p. 422, and Truesdell C.A. and Bharatha S. 1977, *Dedication*.

[41] 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.

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 $t \to -t$.[42]

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 the principle of conservation: conservation and limitation to the efficiency appeared as disconnected requirements.[43]

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[42] 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.

[43] 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 *gratui-*

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.[44]

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.[45]

As Kragh repeatedly pointed out, the second Principle was subject to different interpretations. W. Thomson had "never used the concept

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tement 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."

[44] Stengers I. 2003, pp. 199-200.

[45] 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 Gränzen ihrer Wirkung" can be found in Clausius R. 1864, pp. 322-61.

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".[46]

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 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.

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[46] Kragh H. 2008, pp. 31 and 114-5. Maxwell's specification can be found in Maxwell J.C. 1885, pp. 192-3: see chapter 3 of the present book.

PART I

Two Pathways to Thermodynamics

2. ON THE FIRST PATHWAY: DISCRETE AND CONTINUOUS THEORETICAL MODELS

In September 1859, James Clerk Maxwell, then a young professor of Natural Philosophy at Marischal College in Aberdeen, read a paper at the Meeting of the British Association for the Advancement of Science, held at Aberdeen. The following year the paper was published in the *Philosophical Magazine*, a scientific journal which had already hosted dynamical theories of matter and heat. The paper, the "Illustration of the Dynamical Theory of Gases", consisted of three parts: the first, "On the Motion and Collisions of Perfectly Elastic Spheres", dealt with both mechanical and statistical models of gases. The starting point was the basic assumption of every kinetic theory of heat: matter consists of a huge number of microscopic particles.[1] These "minute parts are in rapid motion, the velocity increasing with the temperature", being the temperature proportional to *vis viva* (or kinetic energy) of such particles. The equation of "perfect gases", as well as other "relations between pressure, temperature and density", could be derived from a theoretical model involving microscopic particles in motion "with uniform velocity in straight lines". In that

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[1] On the relationship between the kinetic theory of gases and existing atomic models, see Brush S.G. 1976, book 1, p. 204: "Although the identification of heat with molecular motion was fairly widely accepted after 1850, many scientists continued to pursue molecular theories which they considered in some way superior to the kinetic theory, though not necessarily denying its applicability for some purposes. The two principal alternatives were the "dynamic" view of the atom as a center of force, and the "atmospheric atom" which exchanged heat vibrations with other atoms through an intermediate ether; while these represented opposing world views, they were often mixed together."

model, the pressure of the gas was the effect of the strikes of the particles "against the sides of the containing vessel".[2]

Maxwell reminded the reader that Clausius had already deduced both the "mean length of path" of a particle and the "distance between the centres of two particles when collisions take place". He intended to further explore Clausius' theoretical investigation, which was based on "strict mechanical principles". His specific theoretical model was based on "an indefinite number of small, hard, and perfectly elastic spheres acting on one another only during impact".[3]

He relied on a standard scientific method, wherein the results drawn from the model had to be compared with the results of "experiments on gases", in order to ascertain whether "the phenomena of gases" were explained or not by the model. The purely kinetic model could be replaced by a *dynamical* model: instead of "hard, spherical and elastic" particles in motion, the reader could imagine particles as "centres of forces". The fact is that the two models stemmed from very different conceptual representations: matter and motion on the one hand, and matter and forces on the other. Although two different *mechanical* traditions were involved, at that stage Maxwell did not seem worried by the theoretical mismatch. He claimed it was "evident" that a suitable arrangement of the second model could lead to results quite close to the first. He imagined a force which was "insensible except at a certain small distance", when it "suddenly appears as a repulsive force of very great intensity". He did not give mathematical details, so that the reference to the second model was purely quali-

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[2] With regard to the intellectual context of Maxwell's first *dynamical* theory of gases, S. Brush remarked that "Maxwell announced his statistical theory of molecular velocities in the same year (1859) that Darwin published his *Origin of Species* based on the assumption that random variations are the driving force in evolution". He went on noting that "Maxwell presented a critical analysis of the kinetic theory at the same meeting of the British Association for the Advancement of Science", which took place at Oxford in 1860, "where Darwin's theory was dissected in the famous Huxley-Wilberforce debate". See Brush S.G. 1978, p. 13.

[3] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p. 377. That the elasticity of a gas could be explained by the elasticity of its microscopic solid elements, or that "the elasticity of a solid atom is in less need of explanation than that of a bulky gaseous body", seemed questionable to many scholars. See Stallo J.B. 1882, p. 128. See also Bridgmann P.W. 1961, pp. 8 and 106-7, and Brush S.G. 1978, p. 100.

tative. Then he proceeded to develop “the assumption of perfectly elastic spherical bodies”.[4]

The subject was arranged in a series of “Propositions”. After having analysed a collision between two spheres “moving in opposite direction with velocities inversely as their masses”, Maxwell inquired into the effect of many collisions on the distribution of *vis viva* among the particles of a gas. He was looking for “some regular law”, allowing him to compute “the average number of particles whose velocity lies between certain limits”. He defined a function $f(x)$ such that $N f(x)\,dx$ was the number of particles whose velocity lay between x and $x+dx$, where $f(x)$ was the fraction of such particles, N the total number of particles, and x, y, z the Cartesian components of particle velocity. He thought that “the existence of the velocity x does not in any way affect that of the velocities y or z”, since the three components are “all at right angles to each other and independent”. According to that hypothesis, Maxwell wrote down the number of particles in a gas whose velocity “lies between x and $x+dx$, and also between y and $y+dy$, and also between z and $z+dz$:

$N f(x) f(y) f(z)\, dx\, dy\, dz$.[5]

Another simplification arose from the rotational symmetry in the space of velocities: the law of the distribution of velocities had to be insensitive to the direction of velocities .

> But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is
> $$f(x)\,f(y)\,f(z)=\phi\left(x^2+y^2+z^2\right).$$
> Solving this functional equation, we find
> $$f(x)=C\,e^{Ax^2}, \qquad \phi(r^2)=C^3\,e^{Ar^2}.$$[6]

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[4] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p. 378. Clausius had already shown that, in the case of non-spherical particles, “the rotatory motion of the system” should also be taken into account, and rotation would “store up a certain proportion of the whole *vis viva*”. In the paper, Maxwell treated the more general case in the short third part, “On the Collision of Perfectly Elastic Bodies of any Form”. See *Ibidem*, p. 405.

[5] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 380. The mutual independence among the components does not hold good: the conservation of momentum and energy does not allow us to choose any value of y and z components for whatever choice of x component. See Brush S.G. 1976, book 2, pp. 587-8.

The constant A had to be negative, otherwise the number of particles with a given velocity would dramatically increase with the value of velocity, and the integration over the whole range of velocities would dramatically diverge. After a simple procedure of normalisation, Maxwell obtained

$$f(x) = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{x^2}{\alpha^2}}.$$

The mathematical law for the distribution of velocities in a gas would therefore be nothing else but the statistical law of distribution of casual *errors* in every physical process of measurement.

> It appears from this proposition that the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the 'method of least squares'. The velocities range from 0 to ∞, but the numbers of those having great velocities is comparatively small.[7]

Apart from the soundness of the hypotheses which Maxwell had assumed, in which sense was this kind of law a physical law rather than a simple statistical law? The choice of a function depending only on the square of velocity, for instance, is not without consequences from the dynamical point of view. It means that a time-symmetry is tacitly assumed: transforming t into $-t$, and therefore v into $-v$, the distribution of velocities cannot change. In Maxwell's words, "the direction of motion of every particle … may be reversed without changing the distribution of velocities". In any case, the deduction of the mathematical law of distribution did not involve specific mechanical laws such as, for instance, the laws of elastic collisions. It involved only some global properties or symmetries of a huge number of particles.[8]

Nevertheless, when in the "Proposition VI" Maxwell tried to deduce one of the effects of the drift towards equilibrium, namely the uniform distribution of *vis viva* between two sets of particles having two

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[6] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 381.

[7] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 381.

[8] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 383.

different kinds of mass, he resorted to the laws of mechanics. Let P be the mass of the first kind and p the average velocity in the first set of particles; let Q be the mass of the second kind and q the corresponding average velocity. After the impact between two particles of different kinds, masses and velocities became p' and q'. In a few passages Maxwell showed that, after the first impact, the expression $\left(Pp^2 - Qq^2\right)$ underwent a progressive decrease, and leads to the equalisation of *vis viva*. We see that a global macroscopic approach, relying on statistical laws, was put forward alongside a local microscopic approach, relying on mechanical laws. The above demonstration could represent an attempt to bridge the gap between mechanics and statistics, but was not so general.[9]

Among Maxwell's notes and drafts stored in Cambridge University Library there are few references to the law of the distribution of velocities. In a manuscript which could be dated between 1862 and 1866, "On the Conduction of Heat in Gases", we find that, if a great number of particles "are in motion in the same vessel", they cannot have the same velocity, but "the average number of particles whose velocity lies within the limits v and $v+dv$" will follow the well-known law of errors

$$N \frac{4}{\alpha^3 \sqrt{\pi}} v^2 e^{-\frac{v^2}{\alpha^2}} dv,$$

where N is the number of particles, and α a constant with the physical dimension of velocity. He specified that "velocities range through all possible values" even though "more particles have a velocity = α than any other given velocity". The fact that, in the manuscript, he spoke of "particles", "elastic spheres" and "small elastic particles" rather than "molecules" suggests that he was dealing with a

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[9] Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, pp 383-4. In the specific case of one-dimension collisions between molecules with the same mass, the term involving masses vanishes, and it would lead to an equalisation of *vis viva* just after the first bump. This is not consistent with the well-known behaviour of these particles: they simply exchange their velocities. The fact is that the demonstration contains an additional hypothesis, namely a "right angle" between the velocities "before impact": this undermines its generality.

mathematical model which, from the outset, was imagined as a statistical ensemble following the Gaussian law of errors.[10]

In another manuscript, "Encounter of Two Molecules", Maxwell insisted on "a step of philosophical importance" which "cannot be overestimated", namely the passage from "absolute certainty" to "high probability". When we are dealing with a "medium" consisting of "multitudes of moving molecules", we have to cope with "our limited powers of observation and even of imagination". These limitations force us "to abandon the strict dynamical method" and "to adopt the statistical method". If the former would require the knowledge of "the course of every molecule", the latter consisted in "dividing the molecules into groups according to some system", and then "confining our attention to the number of molecules in each group". According to Maxwell, the passage from "the motion of a single molecule" to "groups of molecules" entailed the passage from "axioms absolutely certain" to "nothing more than a high probability".[11] Here Maxwell did not specify what kind of uncertainty he was dealing with. In other words, did statistical methods correspond to an intrinsic lack of knowledge, or to the necessity of facing an extremely complex system?

In the following passages of the manuscript, Maxwell made reference to an intermediate spatial dimension, to be found between the microscopic level of molecules and the macroscopic level of the whole gas. He focused on "a group of molecules" contained in "a given region bounded by a closed surface", a mathematical abstraction indeed, which was "large enough to contain a very great number of molecules". It seems that, in some way, Maxwell tried to bridge the gap between the physics of particles and the physics of continuous media. Accordingly, a sort of conceptual bridge between actions at a distance and contiguous actions was outlined. In fact, he imagined the action going on between "the group of molecules" and the surrounding molecules as an action taking place "through the bounding surface" or "through a small portion of the bounding surface". The transfer of matter and energy did not prevent "[t]he state of the medium"

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[10] *Maxwell Manuscript Collection*, Cambridge University Library; reproduced in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, pp. 339-40.

[11] *Maxwell Manuscript Collection*, in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, p. 400.

from remaining "the same"; it was exactly that continuous transfer, involving a huge number of molecules, which let the gas reach its state of "movable equilibrium as regards the matter, the momentum, and the energy". The gas would experience local and *continuous* fluctuations ruled by some *continuous* law. But, shortly afterward, he took into account the effects on a molecule due to "the action of another molecule which comes near it in its course". He put forward a simplified model of collision between a couple of molecules, namely "two molecules moving with equal momentum in opposite directions", in order to let their centre of mass at rest".[12]

The physical picture we receive from these passages is a sort of precarious balance between different theoretical models. On the one hand, discrete events, taking place at the microscopic level, and ruled by the laws of mechanics; on the other hand, continuous distributions and exchanges of velocities which took place at a greater spatial scale, and were ruled by the laws of statistics and probability.

After seven years, Maxwell published a more massive and demanding paper, "On the Dynamical Theory of Gases", in the *Philosophical Transaction*, the official review of the Royal Society.[13] The subject was introduced by nine pages of general remarks and historical notes on matter, elasticity and kinetic theory. A series of short sections followed, covering many issues, from dynamical action between two molecules to diffusion, viscosity and thermal conductivity in a gas. In the first lines of the paper, Maxwell mentioned the long-lasting competition between the two general models of matter: matter as a continuous medium, and matter endowed with a discrete, *molecular* structure. He assumed that molecules moved along "sensibly rectilinear" paths before entering "the sphere of sensible action of the neighbouring molecules". Starting from this theoretical model, Maxwell felt he was able to account for the law of gases and their known physical and chemical features.

> I propose in this paper to apply this theory to the explanation of various properties of gases, and to shew that, besides accounting for the relations of pressure, density, and temperature in a single gas, it affords a mechani-

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[12] *Manuscript Collection*, in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, pp. 401-2.

[13] In 1860 Maxwell had been appointed to the chair of Natural Philosophy at King's College in London, but in 1865 he left London and returned to his Scottish estate.

> cal explanation of the known chemical relation between the density of a gas and its equivalent weight, commonly called the Law of Equivalent Volumes. It also explain the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases.[14]

After having acknowledged the role of Clausius in the establishment of "the most complete dynamical theory of gases", Maxwell faced another long-lasting competition between general theoretical models regarding interactions: discontinuous impacts or continuously acting forces. Some experiments on viscosity had led him to prefer a dynamical approach to a purely kinetic one, and to choose a precise mathematical law of force.

> In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules repelling one another with a force whose direction always passes very nearly through the centres of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance.[15]

The effect of this kind of force would be "the deflection of the path of one particle by another when they come near one another". According to Maxwell, the huge number of subsequent deflections led to a completely disordered, spatial distribution of molecular velocities. In this model, viscosity consisted of a local drift of layers of molecules endowed with different velocities: it appeared as an effect to be found at an intermediate spatial scale, between the macroscopic scale of the whole gas, and the microscopic scale of interacting molecules.[16]

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[14] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 27.

[15] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 29. On the reaction to Maxwell's second theory in German speaking countries, Brush remarked that "Maxwell's new viscosity theory was also disturbing on theoretical grounds". The fact is that "Maxwell's first theory" was "based on the elastic-sphere model", and "Maxwell's switch to … a completely incompatible hypothesis", namely "the model of the atom as a point center of force" appeared quite puzzling. See Brush S.G. 1976, Book 2, p. 441.

[16] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 30.

He was not completely satisfied by the hypothesis that the gas deserved a microscopic analysis, whilst the vessel did not. He imagined a rectangular vessel "with perfectly elastic sides", with molecules which had "no action on one another": molecules could not collide with each other or "cause each other to deviate from their rectilinear paths". In such a model, the vessel was not looked upon as a mere geometrical entity any more. It became a *physical* entity, and its complex interaction with the gas could not be neglected. The pressures on the different sides of the vessel would become "perfectly independent of each other", so that the vessel could experience different tensions in different directions of space. In some way, the gas would not behave as a fluid but as "an elastic solid". The "rigidity", or the elastic reaction of the system gas-vessel, Maxell concluded, "cannot be directly observed" just because of the mechanism of equalisation of pressures in all directions represented by molecular collisions which "deflect each other from their rectilinear courses". The equalisation could not be an instantaneous process: the transient inequality of pressure corresponded to "the phenomenon of viscosity". Another effect of molecular collisions, "when molecules of different kinds are present", was the equalisation of *vis viva* among the different kinds.[17]

In the last two pages of introductory remarks, Maxwell devoted some passages to the concept of "molecule". He held that, in his model of gas, molecules were "those portions of it which move about as a single body". There were models of molecules as "mere points", or "pure centres of force endowed with inertia", but also models with internal structure, for instance a collection of "several such centres of force, bound together by their mutual actions". On the other hand, we could imagine molecules as "small solid bodies of a determinate form", but a new query would arise from this specific model: what kind of new forces should we imagine, in order to bind "the parts of

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[17] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 32-3. With regard to the representation of a gas as a solid, Brush, Everitt and Garber remarked that, "if a fluid ever acts like a solid, it would only do so at high densities", whereas Maxwell "discovered" that "[a] rarefied gas behaves like an elastic solid"! (Brush S., Everitt C.W.F. and Garber E. 1986c, p. 25) The fact is that the connection between gas and vessel, and not the gas in itself, behaved like a solid. The asymmetry between the microscopic structure of gases and the macroscopic geometry of vessels could be traced back to Daniel Bernoulli's eighteenth-century model. See Cercignani C. 1997, p. 44.

these small bodies together"? In this case, Maxwell remarked, "a molecular theory of the second order" would be required. In any case, without giving further details on the structure of molecules, he took for granted that their energy could be split into two parts: the energy of their centres of mass, and the energy of rotations or oscillations around the centres of mass. As a consequence, a collision between two molecules would entail a re-distribution of these two components of energy. In the model of molecules as centres of force, the second component could not come into play, but in the other models it could not be neglected. Nevertheless Maxwell thought he could resort to one of Clausius' previous hypotheses, namely that the two components had, on average, a well-defined ratio "depending on the nature of the molecules".[18]

In the following sections, Maxwell undertook two different pathways: the study of the interactions between couples of molecules, and the search for the law ruling the distribution of velocities among the molecules. In the first section, "On the Mutual Action of Two Molecules", he assumed explicitly that molecules were "simple centres of force", and that the force acting on a couple made them describe "a plane curve" around their centres of mass. This is not, of course, the purely kinematic model put forward in 1860: now intermolecular forces were at work. The dynamical analysis started from two molecules travelling on straight lines, and then undergoing a sudden repulsive force. If their velocities allowed them "to carry them out of the sphere of their mutual action", they departed from the interaction, following a progressively rectilinear path defined by two asymptotes. The curves described by the two molecules should be "symmetrical with respect to the line of apses". The motion of a couple was specified by two geometrical parameters: the distance b "between two parallel asymptotes, one in each orbit", and the angle θ between the pair of asymptotes and the line of apses. Besides the geometrical parameter Maxwell introduced a physical parameter, the relative velocity V between the two molecules. He arranged the three parameters in such a way that the angle θ was a function of b and the relative velocity:

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[18] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 33-4.

the form of the function depended on the law of force between the molecules.[19]

According to Maxwell, the solution of the mechanical problem would proceed through four steps: the determination of V from the velocities of M_2 and M_1, the determination of b, the determination of ϕ, and finally the determination of θ, "if we know the law of force". He imagined a force that acts only during a very narrow interval of time, when the two molecules are very close to each other. Out of this range, the molecules could be looked upon as free molecules. We can disregard, Maxwell wrote, "both the time and the distance described by the molecules during the encounter", when compared with the time spent and the space travelled by the particle outside the range of the repulsive force. A further approximation would require that the fraction of impacts among more than two molecules be really negligible.[20]

In the following section, "On the Mutual Action of Two Systems of Moving Molecules", Maxwell returned to a statistical rather than mechanical approach. On the track of his 1860 paper, he imagined two kinds of molecules in the same vessel, and introduced a function of velocity $f(v)$ whose values corresponded to the statistical weight of the corresponding velocities. Maxwell labelled with N_1 the number of molecules of a certain kind in unit of volume, and N_2 the number of molecules of a different kind, and with (ξ_1, η_1, ζ_1) and (ξ_2, η_2, ζ_2) two specific values of velocity for molecules of the corresponding kind. The mathematical expression

$$dN_1 = f_1(\xi_1;\eta_1;\zeta_1)d\xi_1\, d\eta_1\, d\zeta_1.$$

represented the number of particles of the first kind with velocities in the infinitesimal three-dimensional interval $[\xi_1; \xi_1 + d\xi_1]$, $[\eta_1; \eta_1 + d\eta_1]$ and $[\zeta_1; \zeta_1 + d\zeta_1]$. A similar expression could be written for the number

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[19] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 35-6.

[20] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 37. Maxwell devoted five pages to the procedures of integration with regard to the various parameters. In particular, the integration with regard to the angle θ required the knowledge of the law of force acting between every couple of molecules. Having assumed a force proportional $1/r^n$, experimental data on viscosity suggested $n=5$; from the mathematical point of view, this choice made easier the computation of the mentioned integral. See Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 40-1.

of molecules of the second kind having velocities in the interval $[\xi_2;\xi_2+d\xi_2]$, $[\eta_2;\eta_2+d\eta_2]$ and $[\zeta_2;\zeta_2+d\zeta_2]$. Skipping Maxwell's further three-dimensional computations, I simply quote from his final claim that "the number of encounters of the given kind between the two systems" should be proportional to $dN_1\,dN_2$.[21]

The title of the next section, "On the Final Distribution of Velocity among the Molecules of Two Systems acting on one another according to any Law of Force", seems misleading, since no law of force was involved in the determination of the distribution. He explicitly confined himself to a globally constant distribution over time, wherein "the number of molecules whose velocity lies within given limits remains constant". If a and b were the velocities of two molecules of different kind before the collision, a' and b' the velocities after the collision, and $f(v)$ the required distribution of velocities, then the number of molecules of the first kind, endowed with the velocity a, should have been

$$n_1 = f_1(a)dV,$$

where dV was an element of volume. A similar expression was valid for the molecules of the second kind:

$$n_2 = f_2(b)dV.$$[22]

The key passage consisted of two steps. First, Maxwell assumed that "the number of encounters of the given kind between these two sets of molecules" was proportional to $f_1(a)f_2(b)$. Then he assumed that "the number of pairs of molecules which change their velocities" from a and b to a' and b' was "equal" to the number of couples (or collisions) wherein velocities were transformed from a' and b' into a and b. The first step corresponded to a hypothesis of independence between physical events: the members of a couple had no correlation. Molecules were looked upon as free particles: they had neither interactions nor history. This sounds quite strange from the physical point of

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[21] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 37-8.

[22] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 43-4.

view: collisions are ruled by physical laws, and moreover a definite law of force had been assumed by Maxwell himself. In other words, the statistical approach looks upon molecules and collisions as sets of casual events.[23]

The second step corresponded to a hypothesis of uniformity or equalisation over time: the fluctuations in the distribution of velocities were assumed to preserve the state of equilibrium. In some way, the equilibrium was assumed rather than deduced from the theory. The corresponding relationship,

$$f_1(a)f_2(b)=f_1(a')f_2(b'),$$

together with the principle of conservation of energy,

$$M_1 a^2 + M_2 b^2 = M_1 a'^2 + M_2 b'^2$$

led to distributions of the form

$$f_1(a)=C_1 e^{-\frac{a^2}{\alpha^2}} \quad \text{and} \quad f_2(b)=C_2 e^{-\frac{b^2}{\beta^2}},$$

where $M_1 \alpha^2 = M_2 \beta^2$.

Therefore, "the number of molecules whose component velocities are between" $\xi_1 \, and \, \xi_1 + d\xi_1$, … $[\xi_1 ; \xi_1 + d\xi_1]$, $[\eta_1 ; \eta_1 + d\eta_1]$ and $[\zeta_1 ; \zeta_1 + d\zeta_1]$was

$$dN_1 = \frac{N_1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{\xi^2+\eta^2+\zeta^2}{\alpha^2}} d\xi \, d\eta \, d\zeta .$$[24]

Even though Maxwell's 1867 deduction of the law of distribution is really different from his 1860 deduction, it makes reference to the

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[23] On the difference between the conditions of independence in Maxwell's 1860 and 1867 papers, see Brush S. 1976, book 2, pp. 587-8.

[24] Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 44-5. Obviously, the hypothesis of statistical independence could not be applied to molecules emerging from a collision. See Cercignani C. 1997, p. 69.

same probabilistic law: the product of probabilities for independent events. As already remarked, he assumed the mutual independence between n_1 and n_2, namely the absence of whatsoever dynamical correlation between the molecules with velocity a and the molecules with velocity b. It seems that Maxwell firmly believed in the necessity of a distribution of the kind *distribution of errors*, pivoted around its average value, and was looking for the best way to deduce it. When he got rid of his 1860 deduction while preserving the same result, no experiment suggested one law of distribution rather than another: he expected a Gaussian law of distribution only on theoretical grounds. The motion of molecules appears locally predictable, and ruled by definite laws of motion, but globally unpredictable, even though it led to a distribution statistically uniform over time.[25]

In the 1870s, the Austrian physicist Ludwig Boltzmann tried to go far beyond Maxwell's microscopic interpretation of equilibrium in rarefied gases: he aimed at inquiring into the processes leading to equilibrium. In the first lines of his 1872 paper "Weiteren Studien über das Wärmegleichgewicht unter Gasmolekülen", he reminded the reader about the foundations of the mechanical theory of heat. Molecules were always in motion, but the motion was invisible and undetectable: only the "average values" could be detected by human senses. Those microscopic undetectable motions gave rise to "well-defined laws" at the macroscopic level, which involved the observed average values.[26]

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[25] Maxwell devoted two papers to gas theory after 1867. Brush, Everitt and Garber remarked that, in the end, "gas theory and electromagnetic theory underwent in Maxwell's hands closely similar developments from the use of a specific model to the successive reformulation of the original ideas in more and more abstract terms". (See Brush S., Everitt C.W.F. and Garber E. 1986c, pp. xvii and xxiii) Although the authors stated that "[t]he attempt with electromagnetic fields was more successful because all known phenomena could be brought within the formulation", Maxwell's more abstract (Lagrangian) approach to electromagnetic phenomena was not so general as the authors claimed. See Stein H. 1981, pp. 311-2, and D'Agostino S. 2000, p. 117.

[26] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 316. The expression *Wiener Berichte* is usually used as a short form for the complete name of the Austrian journal where he published important contributions to Thermodynamics: "Sitzungsberichte der kaiserlichen Akademie der Wissenschaften – mathematisch-naturwissenschaftliche Classe". At the time Boltzmann held the chair of theoretical physics in Graz, and had already published some papers on different subjects. His scientific career began with researches on

A thermodynamic theory required therefore two different levels: a microscopic invisible, and a macroscopic visible one. Statistics and probability could bridge the gap between the two levels. Just at the end of the first page, Boltzmann sharply stated that "[p]roblems emerging from the mechanical theory of heat are probabilistic problems". He claimed that probability did not mean uncertainty: the presence of the laws of probability in the mechanical theory of heat did not represent a flaw in the foundations of the theory. Probabilistic laws were ordinary mathematical laws as certain as the other mathematical laws: we should not confuse an "incomplete demonstration" with a "completely demonstrated law of the theory of probability".[27] Probabilistic laws satisfied the well-known requirements of mathematical laws associated to a physical theory: they had to be logically consistent in themselves, and had to explain, or at least describe, the corresponding physical phenomena.

> Die Bestimmung von Durchschnittswerten ist Aufgabe der Wahrscheinlichkeitsrechnung. Die Probleme der mechanischen Wärmetheorie sind daher Probleme der Wahrscheinlichkeitsrechnung. Es wäre aber ein Irrtum, zu glauben, dass der Wärmetheorie deshalb eine Unsicherheit anhafte, weil daselbst die Lehrsätze der Wahrscheinlichkeitsrechnung in Anwendung kommen. Man verwechsle nicht einen unvollständig bewiesenen Satz, dessen Richtigkeit infolgedessen problematisch ist, mit einem vollständig erwiesenen Satze der Wahrscheinlichkeitsrechnung; letzterer stellt, wie das Resultat jedes anderen Kalküls, eine notwendige Konsequenz gewisser Prämissen dar, und bestätigt sich, sobald diese richtig sind, ebenso in der Erfahrung, wenn nur genügend viele Fälle der Beobachtung unterzogen werden, was bei der enormen Anzahl der Körpermoleküle in der Wärmetheorie immer der Fall ist.[28]

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electricity, in particular the relationship between electromagnetism and optics. Together with other German-speaking physicists (August Föppl for instance), he then introduced Maxwell's electromagnetic theory to the Continental scientific community. See Dugas R. 1959, p. 135, Brush 1976, book 1, p. 244, and Buchwald J.Z. 1985, pp. 189 and 197.

[27] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 317-8.

[28] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 316-7. With regard to the relationship between Boltzmann's and "Laplace's view" ("Laplace'sche Geist"), Cassirer emphasised that "objectivity (Gegenständlichkeit)" or objective "reality (Wirklichkeit)" did not require certainty or exact predictability but simply "legality (Gesetzlichkeit)". (Cassirer E. 1936, p. 194) He assumed that the concept of "physical theory" was close to the concept of "objectivity", and the latter, in its turn, close to the concept of "legality". Probability in

Statistic procedures involved the computation of average values for both “a given molecule over very long time-span”, and “many molecules at a given time”. In other words, the statistical sample required a very great number of molecules, and time-intervals much greater than the time of interaction among the molecules. These requirements seemed to Boltzmann reasonable and intrinsically satisfied by a real gas. The mathematical model he put forward dealt with ideal entities: every molecule was represented by “a single material point”.[29]

He assumed that “every molecule spends most of its time flying with uniform rectilinear motion” but made no assumption about the nature of interactions pushing molecules apart when they came very close to each other. He spoke of “collisions”, even though he did not necessarily make reference to “elastic bodies”, and did not exclude “arbitrary forces” acting between the molecules. Moreover he assumed that the walls of the vessel containing the gas reflected the molecules in accordance with the mechanical model of “elastic balls”. At the same time, he assumed that every direction in space was equally probable for every molecule “after a very long time”, and that “from the outset, every direction was equally probable”. According to Boltzmann’s model, collisions among molecules produced three effects. First, a wide range of velocities was realised in the gas: “all possible velocities, from zero to very high velocities” could be represented. Second, collisions would have allowed the spectrum of velocities to be preserved over time “without any further change”. This is a very important assumption, as Boltzmann imagined that collisions *must* lead to a dynamical equilibrium, to a sort of homeostasis which would have preserved both the variety of motions at the microscopic level, and the equilibrium at the macroscopic level. Third, the mathematical law describing the state of equilibrium corresponded to Maxwell’s law of the distribution of velocities, which was nothing else but the distribution of probability “for the different errors in the theory of least squares method”. The number of molecules “whose velocities laid between v and $v+dv$ was represented by the function

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the context of physics did not represent a problem in itself, provided that probability were ruled by some kind of mathematical law.

[29] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 317-8.

$$F(v) = Av^2 e^{-Bv^2}$$

wherein A and B had constant values.[30]

The pivotal mathematical entity was "the number of molecules whose living force lies between x and $x+dx$, at a given time t, in a given space r": Boltzmann labelled $f(x,t)\,dx$ this differential function. From the mathematical point of view, he had to face a "two-steps task": the "determination of a differential equation for $f(x,t)$", and the subsequent "integration". He assumed that "the variation of the function stemmed only from the collisions" between couples of molecules. The keystone of the whole procedure was therefore the computation of the collisions.[31] That a differential equation, namely a mathematical structure based on a continuous variation over time, depended on intrinsically discontinuous processes like collisions, sounds quite astonishing: much more than the specific mathematical difficulties, this was the crucial challenge Boltzmann had to cope with. The function $f(x,t)$ did not belong to the tradition of mathematical physics: a re-interpretation of the concepts of dynamic equation and time-evolution of a physical system was at stake. That function had to bridge the gap between two different traditions in Mechanics: the laws of scattering between solid bodies, which were confined at the invisible microscopic level of interacting molecules, and the equations of motions, which ruled the macroscopic observable behaviour of the whole gas.

> Wollen wir daher die Veränderung dieser Funktion während einer sehr kleinen Zeit τ erfahren, so müssen wir die Zusammenstöße während dieser Zeit der Betrachtung unterziehen. Betrachten wir einen Zusammenstoß, vor welchem die lebendige Kraft des einen der stoßenden Moleküle zwischen x und $x+dx$, die des anderen zwischen x' und $x'+dx'$ liegt. Dadurch ist natürlich die Natur des Zusammenstoßes noch keineswegs vollkommen bestimmt. Je nachdem derselbe ein zentraler oder mehr oder weniger schiefer ist, kann vielmehr die lebendige Kraft des einen der stoßenden Moleküle nach dem Zusammenstoße noch gar mannigfaltige Werthe haben. Setzen wir voraus, dieselbe liege nach dem Zusammenstoß

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[30] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 318-21.

[31] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 322.

> zwischen ξ und $\xi + d\xi$; dann ist aber die lebendige Kraft des zweiten Moleküls nach dem Zusammenstoße bestimmt. Bezeichnen wir letztere mit ξ', so ist nämlich nach dem Prinzip der Erhaltung der lebendigen Kraft
>
> $$x + x' = \xi + \xi';$$
>
> die Summe der lebendigen Kraft beider Moleküle vor dem Stoße ist gleich der Summe der lebendigen Kraft beider Moleküle nach demselben.[32]

A simple grid allowed Boltzmann to show the structure of the collision under consideration, wherein *a* is the first and *b* the second particle. The collision struck out a particle with living force lying between *x* and $x + dx$: as a consequence, the function $f(x,t)\,dx$ decreases by one.

	a	*b*
Before the collision	$x, x + dx$	$x', x' + dx'$
After the collision	$\xi, \xi + d\xi$	

Boltzmann labelled dn the number of these collisions in the unitary volume in the time τ, and assumed that

$$dn = \tau \cdot f(x,t)\,dx\,f(x',t)\,\psi(x,x',\xi)\,dx'\,d\xi$$

$$\int dn = \tau \cdot dx \int_0^{\infty} \int_0^{x+x'} f(x,t)\,f(x',t)\,\psi(x,x',\xi)\,dx'\,d\xi,$$

after having specified that the function $\psi(x,x',t)$ "depends on the law of interaction" between a couple of particles.[33]

If some collisions destroyed an amount of living force between *x* and $x + dx$, some others could create it: if the term $\int dn$ corresponded to a decrease of the function $f(x,t)\,dx$, there should be a term $\int d\nu$ corresponding to an increase of $f(x,t)\,dx$,

$$d\nu = \tau \cdot f(u,t)\,du\,f(v,t)\,\psi(u,v,x)\,dv\,dx,$$

$$\int d\nu = \tau \cdot dx \int_0^{\infty} \int_0^{x+x'} f(\xi,t)\,f(x + x' - \xi,t)\,\psi(\xi, x + x' - \xi, x)\,dx'\,d\xi,$$

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[32] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 322-3.

[33] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 323-4.

in order that

$$f(x,t+d\tau)\,dx=f(x,t)\,dx-\int dn+\int d\nu .$$[34]

The collisions which contributed to $\int d\nu$ were represented by the grid

	a	b
Before the collision	$u,u+du$	$v,v+dv$
After the collision	$x,x+dx$	

Boltzmann developed the left-hand side of the last equation into a Taylor series:

$$f(x,t)\,dx+\frac{\partial f(x,t)}{\partial t}\,\tau\,dx+A\tau^2\,dx=f(x,t)\,dx-\int dn+\int d\nu ,$$

$$\frac{\partial f(x,t)}{\partial t}=\frac{-\int dn}{\tau\,dx}+\frac{\int d\nu}{\tau\,dx}-A\tau ,$$

and obtained a complex integral-differential equation

$$\begin{aligned}\frac{\partial f(x,t)}{\partial t}=&-\int_0^{\infty}\int_0^{x+x'} f(x,t)\,f(x',t)\,\psi(x,x',\xi)\,dx'\,d\xi\\&+\int_0^{\infty}\int_0^{x+x'} f(\xi,t)\,f(x+x'-\xi,t)\,\psi(\xi,x+x'-\xi,x)\,dx'\,d\xi-A\tau ,\end{aligned}$$

which could be put in a more compact form, after having neglected the vanishingly small quantity τ:

$$\frac{\partial f(x,t)}{\partial t}=\int_0^{\infty}\int_0^{x+x'}\big[f(\xi,t)\,f(x+x'-\xi,t)\,\psi(\xi,x+x'-\xi,x)-f(x,t)\,f(x',t)\,\psi(x,x',\xi)\big]dx'\,d\xi .$$[35]

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[34] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 326-7 and 331.

[35] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 331-2.

He assumed that the function $\psi(x,x',t)$ was symmetric with regard the exchange $x \leftrightarrow x'$, namely,

$$\psi(x,x',\xi) = \psi(x',x,x+x'-\xi),$$
$$(\sqrt{x\,x'}\;\psi(x,x',\xi) = \sqrt{\xi\left(x+x'-\xi\right)}\;\psi(\xi,x+x'-\xi,x).$$

This allowed Boltzmann to give the "fundamental equation for the variation of the function $f(x,t)$" the new form

$$\frac{\partial f(x,t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi,t)}{\sqrt{\xi}} \frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}} - \frac{f(x,t)}{\sqrt{x}} \frac{f(x',t)}{\sqrt{x'}} \right] \cdot \sqrt{x\,x'}\;\psi(x,x',\xi)\, dx'\, d\xi$$

.

Immediately he remarked that the stationary function $f(x,t) = f(x) = C\sqrt{x}\,e^{-hx}$, which was nothing else but Maxwell distribution of velocities, made $\partial f(x,t)/\partial t$ vanish in the above equation. According to Boltzmann the demonstration that $\partial f(x,t)/\partial t = 0$ was "nothing else but" Maxwell's demonstration that the Maxwellian distribution of velocities could not change over time.[36]

Boltzmann aimed at a generalisation of Maxwell's results: starting from "an arbitrary distribution of living force", he wondered "how does it change over time". Perhaps scientists would have expected him to try to solve the above equation, but he undertook an apparent detour, and focussed on another function E generated by $f(x,t)$, and on its time derivative:

$$E = \int_0^\infty f(x,t)\left\{ \log\left[\frac{f(x,t)}{\sqrt{x}} - 1 \right] \right\} dx.$$
$$\frac{dE}{dt} = \int_0^\infty \left\{ \frac{\partial f(x,t)}{\partial t}\left[\log\left(\frac{f(x,t)}{\sqrt{x}} - 1 \right) \right] + f(x,t)\left[\frac{\sqrt{x}}{f(x,t)} \frac{1}{\sqrt{x}} \frac{\partial f(x,t)}{\partial t} \right] \right\} dx.$$
$$= \int_0^\infty \left\{ \frac{\partial f(x,t)}{\partial t}\left[\log\left(\frac{f(x,t)}{\sqrt{x}} - 1 \right) \right] + \frac{\partial f(x,t)}{\partial t} \right\} dx = \int_0^\infty \frac{\partial f(x,t)}{\partial t} \log\left(\frac{f(x,t)}{\sqrt{x}} \right) dx.$$

He then put the expression for $\partial f(x,t)/\partial t$ inside the last integral:

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[36] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 332-4.

$$\frac{dE}{dt}=\int_0^\infty \log\left(\frac{f(x,t)}{\sqrt{x}}\right)dx\cdot\int_0^\infty\int_0^{x+x'}\left[\frac{f(\xi,t)}{\sqrt{\xi}}\frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}}-\frac{f(x,t)}{\sqrt{x}}\frac{f(x',t)}{\sqrt{x'}}\right]$$
$$\cdot\sqrt{x\,x'}\;\psi(x,x',\xi)\,dx'\,d\xi=$$
$$=\int_0^\infty\int_0^\infty\int_0^{x+x'}\left[\frac{f(\xi,t)}{\sqrt{\xi}}\frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}}-\frac{f(x,t)}{\sqrt{x}}\frac{f(x',t)}{\sqrt{x'}}\right]\cdot\log\left(\frac{f(x,t)}{\sqrt{x}}\right).$$
$$\cdot\sqrt{x\,x'}\;\psi(x,x',\xi)\,dx\,dx'\,d\xi$$ [37]

Boltzmann undertook a long and demanding computation, which involved some transformations of the new integral. The transformations consisted in writing the integral in four different ways. The four expressions were nothing else but the same expression referred to different variables, provided that the functions $f(x,t)$ and $\psi(x,x',\xi)$ were invariant under the exchange of kinematic variables. After having put forward a typographic simplification, in order to better appreciate the meaning of transformations,

$$\frac{f(x,t)}{\sqrt{x}}=s,\quad \frac{f(x',t)}{\sqrt{x'}}=s',\quad \frac{f(\xi,t)}{\sqrt{\xi}}=\sigma,\quad \frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}}=\sigma'.$$
$$\sqrt{x\,x'}\;\psi(x,x',\xi)=r,$$

he showed that

$$\frac{dE}{dt}=\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma'-s\,s')\cdot\log(s)\cdot r\cdot dx\,dx'\,d\xi=\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma'-s\,s')\cdot\log(s')\cdot r\cdot dx\,dx'\,d\xi=$$

$$=-\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma'-s\,s')\cdot\log(\sigma)\cdot r\cdot dx\,dx'\,d\xi=-\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma'-s\,s')\cdot\log(\sigma')\cdot r\cdot dx\,dx'\,d\xi$$

,

$$\frac{dE}{dt}=\frac{1}{4}\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma'-s\,s')\cdot\left[\log(s)+\log(s')-\log(\sigma)-\log(\sigma')\right]\cdot r\cdot dx\,dx'\,d\xi$$

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[37] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 335.

$$= \frac{1}{4}\int_0^\infty\int_0^\infty\int_0^{x+x'}(\sigma\sigma' - ss')\cdot\log\left(\frac{s\cdot s'}{\sigma\cdot\sigma'}\right)\cdot r\cdot dx\,dx'\,d\xi.^{38}$$

Simple algebraic conclusions could be drawn from the new form of the pivotal entity *dE/dt*: if $\sigma\sigma' > ss'$, then $\log\left(\frac{s\cdot s'}{\sigma\cdot\sigma'}\right) < 0$; if $\sigma\sigma' < ss'$, then $\log\left(\frac{s\cdot s'}{\sigma\cdot\sigma'}\right) > 0$. In any case, the expression inside the integral is negative, and "the whole integral is necessarily negative": this means that "*E* must necessarily decrease". Boltzmann expected that it approached a minimum value, which corresponded to $dE/dt = 0$. This is a very sensitive issue, because the decrease of a function does not assure the existence of a minimum value. Only in this specific case, $df/dt = 0$, which was satisfied for every stationary function of the kind

$$f(x,t) = f(x) = C\sqrt{x}\,e^{-hx}.$$

If we accept Boltzmann's assumption that the evolution of the physical system leads to $dE/dt = 0$, we must accept that the system approaches Maxwell distribution of velocities.[39]

Boltzmann thought that the mathematical result had a deep meaning in the context of the kinetic theory: there was a mathematical entity *E* which "could only decrease or remain constant in the course of the molecular motion", and this could be interpreted as "an analytic proof of the second principle" of Thermodynamics. The quantity dE/dt could be associated to the integral $\int dQ/T$: he therefore concluded that "$\int dQ/T$ is in general negative, and vanishes in the limiting case of a reversible cyclic process". It seemed to Boltzmann that his interpretation of the second Principle was more general than previous interpretations. In particular, it could account for irreversible processes, just the kind of processes "really taking place in nature", whereas the reversible ones were "purely ideal".[40]

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[38] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 343-4.

[39] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 344-5.

[40] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 345-6.

In the next section of the essay, the problematic link between mathematical algorithms and physical concepts was newly at stake, for Boltzmann transformed his integro-defferential equation into an infinite sum of discrete terms. That a late-nineteenth century physicist trained in the tradition of mathematical physics replaced integrals with infinite sums, seems quite puzzling, even though a discrete mathematical model was in accordance with the physical foundations of the kinetic theory of gases. Boltzmann himself tried to justify his theoreticl choice.

> Die Integrale sind bekanntlich nichts anderes als symbolische Bezeichnungen für Summen unendlich vieler, unendlich kleiner Glieder. Die symbolische Bezeichnung der Integralrechnung zeichnet sich nur durch eine solche Kürze aus, dass es in den meisten Fällen nur zu unnützen Weitschweifigkeiten führen würde, wenn man die Integrale erst als Summen von p Gliedern hinschriebe und dann p immer größer werden ließe. Trotzdem aber gibt es Fälle, in denen die letztere Methode wegen der Allgemeinheit, die sie erzielt, namentlich aber wegen der größeren Anschaulichkeit, in der sie die verschiedenen Lösungen eines Problems erscheinen lässt, nicht ganz zu verschmähen ist.[41]

The new discrete procedure Boltzmann was undertaking required that the variable x, representing the living force of a molecule, could assume only a series of multiple values of a given quantity ε. This is perhaps the most astonishing feature of Boltzmann's new theoretical model: energy, just like matter, could rely on a basic unit. In other words, Boltzmann put forward an atomic or molecular representation of energy alongside an atomic or molecular representation of matter. Here we can appreciate one of the main features of late-nineteenth-century theoretical physics: the explicit awareness that a plurality of theoretical models could account for a given class of phenomena. The continuous function $f(x,t)$ had to be replaced by a series of statistical weights: the number w_1 of molecules with energy ε, the number w_2 of molecules with energy 2ε, and so on. The label $N_{\chi\lambda}^{kl}$ represented "the number of collisions" which transformed the energies $k\varepsilon$ and $l\varepsilon$ of two molecules into the energies $\chi\varepsilon$ and $\lambda\varepsilon$. The principle of the conservation of energy required that

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[41] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 347.

$k + l = \chi + \lambda$.[42]

In Boltzmann's theoretical model, the discrete function $N_{\chi\lambda}^{kl}$ depended on the weights w_k and w_l, on the time span τ, and on a function $A_{\chi\lambda}^{kl}$, according to the equation

$$N_{\chi\lambda}^{kl} = \tau \cdot w_k \cdot w_l \cdot A_{\chi\lambda}^{kl}.$$

The above equation was the discrete analogous of the equation $dn = \tau \cdot f(x,t)\, dx\, f(x',t)\, \psi(x,x',\xi)\, dx'\, d\xi$, and the functions $A_{\chi\lambda}^{kl}$ were the discrete analogous of the continuous function $\psi(x,x',t)$. The discrete analogous of the symmetries involving ψ led Boltzmann to define a new function $B_{\chi\lambda}^{kl} = \sqrt{kl}\, A_{\chi\lambda}^{kl}$, which transformed the above equation into

$$N_{\chi\lambda}^{kl} = \tau \cdot \frac{w_k w_l}{\sqrt{kl}} \cdot B_{\chi\lambda}^{kl}.$$

$B_{\chi\lambda}^{kl}$ was the discrete analogous of the continuous function $\sqrt{x\,x'}\, \psi(x,x',\xi)$, and enjoyed the same properties of symmetry $B_{\chi\lambda}^{kl} = B_{kl}^{\chi\lambda}$.[43]

The collisions were the only processes which could change the statistical weights w_p. For instance, the weight w_1 increased because of collisions creating a molecule with energy ε, and decreased because of collisions destroying the energy ε:

$$\begin{aligned} w_1' = w_1 &- N_{22}^{13} - N_{23}^{14} - N_{32}^{14} - N_{24}^{15} + \ldots\ldots \\ &+ N_{13}^{22} + N_{14}^{23} + N_{14}^{32} + N_{15}^{24} + \ldots\ldots \end{aligned}.$$

Once again, Taylor's development allowed Boltzmann to write $w_1' = w_1 + \tau \dfrac{dw_1}{dt}$, and

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[42] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 348-9.

[43] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 349-50.

$$\frac{dw_1}{dt} = -\frac{w_1w_3}{\sqrt{1\cdot 3}}\cdot B^{13}_{22} - \frac{w_1w_4}{\sqrt{1\cdot 4}}\cdot B^{14}_{23} - \frac{w_1w_4}{\sqrt{1\cdot 4}}\cdot B^{14}_{32} - \frac{w_1w_5}{\sqrt{1\cdot 5}}\cdot B^{15}_{24} - \ldots\ldots$$
$$+\frac{w_2w_2}{\sqrt{2\cdot 2}}\cdot B^{22}_{13} + \frac{w_2w_3}{\sqrt{2\cdot 3}}\cdot B^{23}_{14} + \frac{w_3w_2}{\sqrt{3\cdot 2}}\cdot B^{32}_{14} + \frac{w_2w_4}{\sqrt{2\cdot 4}}\cdot B^{24}_{15} + \ldots\ldots$$[44]

A transformation of the couple of weights w_k and w_l, which was nothing else but the reverse of the transformation of $A^{kl}_{\chi\lambda}$, led Boltzmann to define the new weights $u_k = \frac{w_k}{\sqrt{k}}$ and the new equations

$$\frac{du_1}{dt} = \left(u_2^{\,2} - u_1u_3\right) B^{13}_{22} + \left(u_2u_3 - u_1u_4\right)\cdot\left(B^{14}_{23} + B^{14}_{32}\right) + \ldots\ldots$$
$$\sqrt{2}\,\frac{du_2}{dt} = 2\left(u_1u_3 - u_2^{\,2}\right) B^{13}_{22} + \left(u_1u_4 - u_2u_3\right)\cdot\left(B^{14}_{23} + B^{14}_{32}\right) + \ldots\ldots$$
$$\ldots\ldots \quad \ldots\ldots$$
$$\sqrt{p}\,\frac{du_p}{dt} = \left(u_2u_{p-1} - u_1u_p\right)\cdot\left(B^{1,p}_{2,p-1} + B^{1,p}_{p-1,2}\right) + \ldots\ldots$$

If we compare the last equations, which stemmed from a discrete model, with the equation for $\partial f(x,t)/\partial t$, which stemmed from a continuous model, we find a system of p ordinary differential equations instead of a single complex integral-differential equation.[45]

Following the analogy with the continuous function $f(x,t)$, Boltzmann defined the function

$$E = u_1\cdot\log(u_1) + \sqrt{2}\,u_2\cdot\log(u_2) + \sqrt{3}\,u_3\cdot\log(u_3) + \ldots\ldots + \sqrt{p}\,u_p\cdot\log(u_p),$$

and its time derivative dE/dt. In order to shorten the length of the demonstration, Boltzmann confined himself to the first three terms in the above equations: the structure of the demonstration was not modified by this simplification. If

$$\frac{du_1}{dt} = \left(u_2^{\,2} - u_1u_3\right) B^{13}_{22}, \qquad \sqrt{2}\,\frac{du_2}{dt} = 2\left(u_1u_3 - u_2^{\,2}\right) B^{13}_{22},$$
$$\sqrt{3}\,\frac{du_3}{dt} = \left(u_2^{\,2} - u_1u_3\right) B^{13}_{22}$$

---

[44] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 351-2.

[45] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 353.

then

$$
\begin{aligned}
\frac{dE}{dt} &= \left(u_2{}^2 - u_1 u_3\right) B_{22}^{13} \cdot \left[\log(u_1) - 2\log(u_2) + \log(u_3)\right] \\
&= B_{22}^{13} \cdot \left(u_2{}^2 - u_1 u_3\right) \log\left(\frac{u_1 u_3}{u_2{}^2}\right).
\end{aligned}
$$
[46]

This was the crucial step in Boltzmann's demonstration in the context of the discrete model: the structure of this equation was not so different from the structure of the corresponding continuous equation. He could therefore repeat those algebraic remarks: if $u_2{}^2 > u_1 u_3$ then the second term is positive, and the third negative; if $u_2{}^2 < u_1 u_3$, then the second is negative, and the third positive. In any case, the derivative dE/dt is negative, unless $u_2{}^2 = u_1 u_3$, which entails $dE/dt = 0$. Boltzmann concluded that the function E was decreasing, and assumed that it approached "its minimum value".[47]

After having faced the case of polyatomic molecules, he came back to the relationship between the function E and the entropy in the case of mono-atomic gases "whose atoms have realised the thermal equilibrium". He returned to the continuous model, and chose the distribution of velocities

$$
f^* = \frac{1}{V\left(\frac{4\pi T}{3m}\right)^{3/2}} e^{-\frac{3m}{4T}\left(u^2 + v^2 + w^2\right)},
$$

where V was the volume of the gas, and m and T the mass and average energy of an atom. In this case the function E^* becomes

$$
E^* = N \iint f^* \log\left(f^*\right) dx\,dy\,dz\,dv\,du\,dw = -N \log\left[V\left(\frac{4\pi T}{3m}\right)^{3/2}\right] - \frac{3}{2}N,
$$

---

[46] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 354.

[47] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 355.

and "corresponds to the entropy of a mono-atomic gas, apart from a constant factor and addend".[48]

In conclusion, two important features of Boltzmann's theoretical pathway deserve to be emphasised. First, Boltzmann forced Mechanics and Statistics to stay beside each other. Second, he gave up the demand that the behaviour of a physical system as a whole be reduced to, and explained by, the behaviour of its components. Every molecular component followed the laws of ordinary mechanics, but the whole followed statistical laws: the whole could not be looked upon as a mere sum of its microscopic parts.[49]

The apparent contradiction between the reversibility of individual collisions and the irreversibility of global evolution, which stemmed from the hypothesis of dynamical independence of the molecules, raised some debate. Some physicists began to wonder what would have happened if we had managed to instantaneously reverse the velocity of every molecule. Would the system go upstream, and therefore away from equilibrium? Before taking a look at that debate, we can say that no series of collisions among dynamically independent molecules could send Boltzmann's physical model backwards, apart from the huge amount of energy and information required in order to perform the hypothetical inversion.[50]

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[48] Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 399-400.

[49] In this conceptual gap, Cassirer saw a deep transformation of "the ideal of knowledge". See Cassirer E. 1936, p. 97: "Denn eben der Umstand, dass so weitreichende Aussagen über ein physikalisches Ganze unter Verzicht auf die Kenntnis der einzelnen Teile möglich sind, stellt vom Standpunkt der reinen Punktmechanik eine Paradoxie dar und enthält eine Umbildung des Erkenntnisideals, das sie bisher durchgeführt hatte."

[50] With regard to criticism about Boltzmann theory, in particular Loschmidt criticism, see Dugas R. 1959, pp. 160 and 180, Brush S.G. 1976, Book 1, p. 239, and Badino M. 2005, p. 77.

3. SWINGING BETWEEN MECHANICAL MODELS AND PROBABILITY

In 1872, after his return to Cambridge, in the treatise *The Theory of Heat*, Maxwell widened his perspective, and inquired into the different aspects of Thermodynamics. Unfortunately, when he focused on the recently established concept of "entropy", he gave it a different meaning: Maxwell's entropy was different from Clausius' "Entropie" even from the dimensional point of view. In the simple case of a vessel containing a gas, Maxwell's "entropy" was "only a part of the intrinsic energy of the system": it was the part which "is capable of being converted into mechanical work by actions going on within the vessel", provided that "any communication with external space by the passage either of matter or of heat" was excluded. In brief, entropy was for Maxwell "the Available Energy of the system". He pointed out that Clausius had made use of the same name for "the remainder of the energy, which cannot be converted into work". Nevertheless, he had found it "more convenient to adopt the suggestion of Professor Tait, and give the name of Entropy to the part which can be converted into mechanical work." In the case of gases, Maxwell's entropy vanished when "the pressure and temperature of the system have become uniform". The total energy of the system could be looked upon as "the sum of the entropy and the energy remaining in the state of uniform pressure and temperature". The decrease of the entropy could be the result of "the conduction and radiation of heat from one part of the system to another", for conduction and radiation reduced "the difference of temperature between the parts of the system". In any case, the whole energy could not change: it was "indestructible", and it maintained its seat inside the system, provided that it had not been "removed from the system" itself.[1]

Both the transfer of matter and energy could decrease the content of entropy of a given system. Maxwell found it possible "to prevent material communication between the parts of a system", but he found it impossible "to prevent thermal communication". This meant that "the entropy of every system is in a state of decay unless it is supplied from without". According to Maxwell, that impossibility had been theoretically translated into "Thomson's doctrine of the Dissipation of Energy", where "dissipated" energy was nothing else but the energy which "cannot be rendered available as mechanical energy". It had been Thomson to put forward the "theory of entropy" in 1853, even though "the name" had been "first employed by Clausius in 1854". In brief, Maxwell saw a fundamental "natural fact" and different theoretical interpretations of it, which were endowed "with increasing degrees of scientific completeness". At a basic level he saw the "law of communication of heat", then "the principle of Carnot, and the second law of thermodynamics", and finally "the theory of Dissipation of Energy".[2]

He attributed "the recent development of the dynamical theory of gases" to Clausius, and stressed the deep similarity between the "distribution of the molecules according to their velocities", the distribution of "bullet-holes in a target according to their distances from the point aimed at", the phenomenon of "heat diffusion from a hot stratum by conduction", and in general "the distribution of observations according to the magnitude of their errors". What the mentioned configurations had in common was a sort of inescapable randomness, which was due to incomplete knowledge of the corresponding processes. He found that those "physical phenomena" involved causes "over which we have no control": from his point of view, "a scattering of particles of matter, a deviation of observations from the truth,

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[1] Maxwell J.C. 1872, pp. 186-7. See p. 186: "DEFINITION OF ENTROPY. – *The Entropy of a system is the mechanical work it can perform without communication of heat, or alteration of its total volume, all transference of heat being performed by reversible engines.*" In 1871 Maxwell had accepted the offer from Cambridge to become the first Professor of Physics at the Cavendish Laboratory.

[2] Maxwell J.C. 1872, pp. 188.

or a diffusion of velocity or of heat" had to be expressed by the same mathematical law.[3]

Maxwell acknowledged that his statistical approach was in opposition to "the strict kinetic method of tracing the exact circumstances of each individual molecule". The results of statistical procedures could account for the behaviour of the gas as a whole, but had nothing to say on the behaviour of "each molecule". In brief, he acknowledged that mechanical and statistical methods dealt with two different sets of information. When we follow the global behaviour of a gas, "we do not perceive the individual molecules", and we part with the basic tool-box of Mechanics, namely exact paths in space and time, and differential equations. In Maxwell's words, we are compelled to "abandon the strict dynamical method, in which we follow every motion by the calculus".[4]

He wondered whether a set of molecules had something in common with a population of living beings belonging to a given species. He first noted that "there is a perpetual generation and destruction of the individuals of which the species consist": in the context of the sciences of life, processes like "generation, variation, and discriminative destruction" made sense. This was not the case for molecules: they were "permanent", unaffected by "generation or destruction", and could not undergo "variation", because any difference "between the individuals of each species" was excluded. Molecules appeared as "unalterable by any of the processes which go on in the present state of things". Moreover, "every individual of each species is exactly of the same magnitude", and those individuals "also agree in the nature of the light which they emit – that is, in their natural periods of vibration", in accordance with known experiments. Maxwell's treatise ended with the open question if some process leading to the elimination of "every molecule whose mass differs from that of some one of our so-called elements" had ever taken place. The time required seemed definitely too long, and exceeding "the utmost limits ever demanded by evolutionists as many times as these exceed the period of vibration of a molecule".[5]

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[3] Maxwell J.C. 1872, pp. 285 and 289.

[4] Maxwell J.C. 1872, pp. 288-9 and 309.

[5] Maxwell J.C. 1872, pp. 310-12.

In 1873, Maxwell wrote some informal papers on the foundations of science: three of them have been preserved, and were published in 1882, in Maxwell's scientific biography edited by Campbell and Garnett. The first paper dealt with the dichotomy Necessity-Contingency in the natural world, and contained some references to the question of "the Freedom of Will". More specifically, Maxwell's cogitations pivoted around the concept of statistical law, and around the behaviour of complex systems in which past or future states were largely unpredictable. He was aware that he was handling very sensitive issues, which involved both physics and philosophy: conclusive answers could not be expected, even though it was "absolutely manifest" that "any development of physical science is likely to produce some modifications of the methods and ideas of philosophers".[6]

According to Maxwell, the progress of "molecular science" had forced "on our attention the distinction between two kinds of knowledge", which he termed "the Dynamical and the Statistical". Even though "statistical matter" was definitely "within the province of human reason", and "valid consequences" could be deduced "from it by legitimate methods", their results belonged "to a different department of knowledge from the domain of exact science". The two methods stemmed from the different features of the microscopic and macroscopic level of investigation. He pointed out that a "constituent molecule of a body has properties very different from those of the body to which it belongs: apart from their "immutability" and other "recondite properties", molecules had velocities which were "different from that which we attribute to the body as a whole".[7]

The results of statistical or non-exact science were not "symmetrical functions of time": in particular, some kind of uncertainty emerged when we tried to deduce "the past state or the future state of things from the known present state". He termed "historical" the inquiry directed towards the past, and "prophetical" that directed towards the future. If astronomy was the best instance of symmetrical behaviour with regard to time, "in the theory of the diffusion of matter, heat, or motion" the prophetical problem was "always capable of solution",

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[6] Maxwell J.C. 1873a, in Campbell L. and Garnett W. 1882, pp. 434-7. I thank Simcha Rozen for having drawn my attention to Maxwell's remarks on "determinism".

[7] Maxwell J.C. 1873a, in Campbell L. and Garnett W. 1882, pp. 438-40.

but the "historical one" was generally "insoluble". He imagined complementary situations "in which the past, but not the future" might be "deducible by the present": it was the case of physical systems affected by instability, where "an infinitely small variation of the present state" might bring about "a finite difference in the state of the system in a finite time". From a philosophical point of view, if stability made reference to "[t]he doctrine of Determinism", instability made reference to "[t]he doctrine of free will". From a specifically physical point of view, instability was at stake in phenomena like explosions: in such cases, "the system has a quantity of potential energy", which can be transformed "into motion", but the transformation cannot take place until "the system has reached some configuration". That configuration required "an expenditure of work", which could be "infinitesimally small", and in general bore "no definite proportion to the energy developed" in the subsequent process of explosion.[8]

In such cases, there were some energy thresholds, and the system was extremely sensitive to infinitesimal variations of energy around the threshold values. Maxwell acknowledged that there were in nature "more singular points" than expected by the study of simplified mathematical models, which corresponded to physical systems endowed with "lower organisation". In singular points, or points of instability, "prediction" became "impossible", unless we had "absolutely perfect data" at our disposal, and were "guided by the omniscience of contingency". In the end, Maxwell remarked that "the study of singularities and instabilities, rather than the continuities and stabilities of things" might "tend to remove the prejudice in favour of determinism". By an enigmatic skip from the theoretical to meta-theoretical level, he guessed that determinism had probably been born "from assuming that the physical science of the future is a mere magnified image of that of the past".[9]

In the same year Maxwell specified his concept of "molecule" and "atom". In 1873, in a short paper published in *Nature*, he wondered whether matter could be infinitely divisible. He stated that "(a)ccording to Democritus and the atomic school, we must answer in the negative", and that the answer was common to "the atomic doc-

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[8] Maxwell J.C. 1873a, in Campbell L. and Garnett W. 1882, pp. 440-41 and 443.

[9] Maxwell J.C. 1873a, in Campbell L. and Garnett W. 1882, pp. 444.

trine of Democritus, Epicurus, and Lucretius, and, I may add, of your lecturer". In 1875, when he wrote the voice "Atom" for the *Encyclopaedia Britannica*, he upheld the theoretical model of atom as a hydrodynamic ring. He stated that, although the "small hard body imagined by Lucretius, and adopted by Newton, was invented for the express purpose of accounting for the permanence of the properties of bodies", it failed "to account for the vibrations of a molecule as revealed by the spectroscope". On the contrary, "the vortex ring of Helmholtz, imagined as the true form of atom by Thomson, satisfies more of the conditions than any atom hitherto imagined". According to Maxwell, the main satisfactory features of the model were its "permanent" and, at the same time, pliable structure.[10]

In 1877 Boltzmann published an even longer paper, where he reminded the reader that the function *E* he had introduced in 1872 could never increase, and that it reached its minimum value at thermal equilibrium. He also reminded the reader about a recently published paper, "Bemerkungen über einige Probleme der mechanischen Wärmetheorie": there he had shown that "there are more uniform than non-uniform distributions" of living force among the molecules of a gas, and that a great probability "that the distribution become uniform over time" followed.[11]

Indeed, the relationship between the second Principle of Thermodynamics and the probability of the distribution of energy was the keystone of Boltzmann's new approach. He started from a series of hypotheses: first, in most cases "the initial state was an improbable one", second, the physical system "hastens towards more probable states", third, it reaches its "most probable state, which corresponds to the thermal equilibrium" at the end of the transformation, and finally, the entropy of the system "can be identified with the probability of the corresponding state".

> Es ist also damit ausgesprochen, daß man den Zustand des Wärmegleichgewichtes dadurch berechnen kann, daß man die Wahrscheinlichkeit der verschiedenen möglichen Zustände des Systems aufsucht. Der Anfangs-

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[10] Maxwell J.C. 1873b, p. 437, and Maxwell J.C. 1875, in Maxwell J.C. 1890, vol. 2, pp. 470-1.

[11] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 164.

> zustand wird in den meisten Fällen ein sehr unwahrscheinlicher sein, von ihm wird das System immer wahrscheinlicheren Zustände zueilen, bis es endlich den wahrscheinlichsten, d.h. den des Wärmegleichgewichtes, erreicht hat. Wenden wir dies auf den zweiten Hauptsatz an, so können wir diejenige Größe, welche man gewöhnlich als die Entropie zu bezeichnen pflegt, mit der Wahrscheinlichkeit des betreffenden Zustandes identifizieren.[12]

His physical model of gas was not so far from the model he had put forward five years before. The gas was "contained in a vessel with rigid and elastic walls", and the molecules interacted as they were equally rigid and elastic balls. Another suitable model was that of "centres of force" endowed with a specific law of force: only when their distances became "less than a given value", they experienced some kind of interaction. This allowed Boltzmann to combine two different processes, which stemmed from two different mechanical traditions: the continuity of unperturbed trajectories, and the discontinuity of sudden collisions.[13]

The molecules could assume only discrete values of velocity: the model was qualified by Boltzmann himself as "fictitious" and "not corresponding to an actual mechanical problem", although "much easier to handle mathematically". The series of available "living forces" corresponded to an "arithmetic progression" $0,\ \varepsilon,\ 2\varepsilon,\ 3\varepsilon,\ \ldots..,\ p\varepsilon$ with an upper bound $P = p\varepsilon$. These values of the energy could be "distributed over the n molecule in all possible ways", provided that the sum of all energies was preserved over time, and assumed a given value $\lambda \cdot \varepsilon = L$.[14]

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[12] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 165. On the new role played by probability in physics, see Prigogine I. and Stengers I. 1986, p. 194: "L'innovation consistait à introduire la probabilité en physique et cela, non pas à titre d'instrument d'approximation mais bien de principe explicatif, à montrer quel comportement nouveau un système peut adopter du fait d'être formé d'une population nombreuse …."

[13] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 166. Dugas reminded us that Boltzmann's theoretical representation of atoms and molecules evolved over time. In the first volume of his *Vorlesungen über Gastheorie* (1895-1898), we find molecules as "elastic spheres" and then molecules as "centres of force", whereas in the second volume, molecules are represented as "mechanical systems characterized by generalized coordinates". See Dugas R. 1959, pp. 25 and 79, footnote 5 included.

[14] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 167-9.

Boltzmann called "complexions" the different distribution of energy among the n molecules, which corresponded to the same number of molecules endowed with a given value of energy. In other words, a complexion was a simple permutation in a fixed state or distribution of energy. If a given state corresponds to " w_0 molecules with null living force, w_1 molecules with living force ε, w_2 with living force 2ε, and so on", there is a given number of complexions corresponding to the state, which Boltzmann labelled "the number of complexions" B or "number of permutations" or "permutability of a given distribution". In his 1877 paper, the *discrete function* B took on the crucial role played by the *discrete function* $N_{\chi\lambda}^{kl}$ in his 1872 paper.[15]

The computation of the "permutability" B was submitted to the conservation of matter and energy:

$$
\begin{aligned}
& w_0 + w_1 + w_2 + \ldots\ldots + w_p = n \\
& 0w_0 + 1w_1 + 2w_2 + \ldots\ldots + pw_p = \lambda \\
& \mathrm{B} = \frac{n!}{(w_0)! \cdot (w_1)! \cdot (w_2)! \cdot \ldots\ldots \cdot (w_p)!}.
\end{aligned}
$$

For every state, the number of complexions corresponded to the number of permutations among all the molecules divided by the number of internal permutations among the members of every set of molecules owning the same energy. We see that a single great value w_k in the denominator of the fraction makes the denominator greater than the case of many little values w_k, provided that the sum of all w_k is n in any case. In other words, a very asymmetric distribution of energy makes the denominator of B a great number, whereas a very symmetric distribution makes the denominator much lesser. This means that the number of complexions B is little for asymmetric distributions of energy, and is great for symmetric distributions.[16]

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[15] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 169-70. At this stage of Boltzmann's theorisation, every specific mechanical model was dismissed. See Campogalliani P. 1992, p. 455: "… in questo ambito ogni modello ancorato alla meccanica delle collisioni molecolari risulta sostanzialmente accantonato …"

[16] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 175-6.

Boltzmann identified the minimum of the denominator with the minimum of its logarithm, because the denominator "is a product" of factorials. The expression to minimise was therefore

$$\begin{aligned} M &= \ln\left[(w_0)!\cdot(w_1)!\cdot(w_2)!\cdot\ldots\ldots\cdot(w_p)!\right] \\ &= \ln\left[(w_0)!\right]+\ln\left[(w_1)!\right]+\ln\left[(w_2)!\right]+\ldots\ldots+\ln\left[(w_p)!\right]. \end{aligned}$$

At this point, he suddenly changed his model, "in order to apply the differential calculus" to a computation based on the discrete structure of integer numbers. He transformed the *factorial function* into the *Gamma function*, which was a generalisation of the *factorial function* to continuous numerical sets. Consistently with the generalisation $\Gamma(w_k+1)=(w_k)!$, the last equation was translated into

$$M_1=\ln\left[\Gamma(w_0+1)\right]+\ln\left[\Gamma(w_1+1)\right]+\ln\left[\Gamma(w_2+1)\right]+\ldots\ldots+\ln\left[\Gamma(w_p+1)\right].$$[17]

The search for the minimum of M_1 was performed by Boltzmann with the help of the Lagrange-multipliers procedure.[18] Another mathematical switch was activated at this point; he re-translated the expression M into a discrete form, making use of the approximation

$$\Gamma(w_k+1)=(w_k)!=\sqrt{2\pi}\left(\frac{w_k}{e}\right)^{w_k}.$$

In this case, the expression to be minimised was

---

[17] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 176. In subsequent years, Boltzmann tried to clarify the conceptual tension between continuous and discontinuous theoretical models. In two papers, first published in the *Annalen der Physik und Chemie* in 1897, and then in his *Populäre Schriften*, he claimed that "[a]tomism seems inseparable from the concept of the continuum". He noticed that in the theory of heat conduction and in the theory of elasticity, "one first imagines a finite number of elementary particles that act on each other according to certain simple laws and then once again looks for the limit as this number increases". In any case, we have to start from "a finite number of elements" even in integral calculus. According to Boltzmann, mathematical procedure required the passage from discontinuous to continuous representations, just in this order. See Boltzmann L. 1897a, p. 44, and Boltzmann L. 1897b, p. 55. On the Kantian *flavour* of Boltzmann's approach to that conceptual tension, see Dugas R. 1959, p. 73.

[18] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 177. From the mathematical point of view, the procedure yields only a necessary condition.

$$
\begin{aligned}
M &= \ln\left[(\frac{w_0}{e})^{w_0} \cdot (\frac{w_1}{e})^{w_1} \cdot (\frac{w_2}{e})^{w_2} \cdot \ldots\ldots \cdot (\frac{w_p}{e})^{w_p} \right] \\
&= \ln(\frac{w_0}{e})^{w_0} + \ln(\frac{w_1}{e})^{w_1} + \ln(\frac{w_2}{e})^{w_2} + \ldots\ldots + \ln(\frac{w_p}{e})^{w_p} \\
&= w_0(\ln w_0 - \ln e) + w_0(\ln w_0 - \ln e) + w_0(\ln w_0 - \ln e) + \ldots\ldots + w_0(\ln w_0 - \ln e) \\
&= w_0 \ln w_0 + w_1 \ln w_1 + w_2 \ln w_2 + \ldots\ldots + w_p \ln w_p - (w_0 + w_1 + w_2 + \ldots\ldots + w_p) \\
&= w_0 \ln w_0 + w_1 \ln w_1 + w_2 \ln w_2 + \ldots\ldots + w_p \ln w_p - n.
\end{aligned}
$$
[19]

Subsequently the quantity ε was interpreted as "a very small quantity", and the frequencies $w_0, w_1, w_2, \ldots\ldots w_p$ were expressed by means of a continuous function *f(x)*:

$$
w_0 = \varepsilon \cdot f(0); \quad w_1 = \varepsilon \cdot f(\varepsilon); \quad w_2 = \varepsilon \cdot f(2\varepsilon); \quad \ldots\ldots\ldots\ldots
$$

The new pathway from a discrete model back to a continuous one required two steps. In the first, he re-introduced the function *f* in the above expression:

$$
\begin{aligned}
M &= \varepsilon f(0) \ln \varepsilon f(0) + \varepsilon f(\varepsilon) \ln \varepsilon f(\varepsilon) + \varepsilon f(2\varepsilon) \ln \varepsilon f(2\varepsilon) + \ldots\ldots + \varepsilon f(p\varepsilon) \ln \varepsilon f(p\varepsilon) - n \\
&= \varepsilon[f(0) \ln \varepsilon f(0) + f(\varepsilon) \ln \varepsilon f(\varepsilon) + f(2\varepsilon) \ln \varepsilon f(2\varepsilon) + \ldots\ldots + f(p\varepsilon) \ln \varepsilon f(p\varepsilon)] - n \\
&= \varepsilon[f(0) \ln f(0) + f(\varepsilon) \ln f(\varepsilon) + f(2\varepsilon) \ln f(2\varepsilon) + \ldots\ldots + f(p\varepsilon) \ln f(p\varepsilon)] + \\
&+ \varepsilon[f(0) \ln \varepsilon + f(\varepsilon) \ln \varepsilon + f(2\varepsilon) \ln \varepsilon + \ldots\ldots + f(p\varepsilon) \ln \varepsilon] - n \\
&= \varepsilon[f(0) \ln f(0) + f(\varepsilon) \ln f(\varepsilon) + f(2\varepsilon) \ln f(2\varepsilon) + \ldots\ldots + f(p\varepsilon) \ln f(p\varepsilon)] + \\
&+ \varepsilon \ln \varepsilon [f(0) + f(\varepsilon) + f(2\varepsilon) + \ldots\ldots + f(p\varepsilon)] - n \\
&= \varepsilon[f(0) \ln f(0) + f(\varepsilon) \ln f(\varepsilon) + f(2\varepsilon) \ln f(2\varepsilon) + \ldots\ldots + f(p\varepsilon) \ln f(p\varepsilon)] + \\
&+ \varepsilon n \ln \varepsilon - n
\end{aligned}
$$
,

and in the fundamental laws of conservation

$$
\varepsilon[f(0) + f(\varepsilon) + f(2\varepsilon) + \ldots\ldots + f(p\varepsilon)] = n
$$

---

[19] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 187-8. He had tried to solve the problem by means of an algebraic variable x, which stemmed from the chain of relationships $w_1 = x \cdot w_0; \quad w_2 = x \cdot w_1 = x^2 \cdot w_0; \quad w_3 = x^3 \cdot w_0; \quad \ldots\ldots$. See Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 178-85.

$$\varepsilon\left[0\cdot f(0)+\varepsilon\cdot f(\varepsilon)+2\varepsilon\cdot f(2\varepsilon)+\ldots\ldots+p\varepsilon\cdot f(p\varepsilon)\right]=L.$$

Boltzmann disregarded the term containing only n and ε, because of their constant value: in particular, ε had "the same value for all the distributions of state". The expression M to be minimized was therefore

$$M'=\varepsilon\left[f(0)\ln f(0)+f(\varepsilon)\ln f(\varepsilon)+f(2\varepsilon)\ln f(2\varepsilon)+\ldots\ldots+f(p\varepsilon)\ln f(p\varepsilon)\right].$$[20]

The second step consisted in replacing the last three sums with infinite integrals:

$$M'=\int_0^\infty f(x)\ln\left[f(x)\right]dx$$

$$n=\int_0^\infty f(x)\,dx$$

$$L=\int_0^\infty x\cdot f(x)\,dx.$$

The procedure of Lagrange's multipliers was on the stage once again, in order to minimize the first integral under the conditions imposed by the second and third. As a solution the usual function emerged, which was interpreted by Boltzmann in the usual way: "at thermal equilibrium, the probability of a living force lying between x and $x+dx$" is

$$f(x)\,dx=Ce^{-hx}\,dx.$$[21]

After having devoted some pages to multi-atomic molecules, and many more pages to analysing different distributions of probability, in the last section Boltzmann faced "the relationship between entropy and distribution of probability". He re-defined "the measure of the permutability" in a slightly different way,

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[20] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 188.

[21] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 188-90. Boltzmann showed that "the second variation of M'" was necessarily positive, and therefore the function really represented a minimum.

$$\Omega=-\iiint\iiint f(x,y,z;u,v,w)\ln[f(x,y,z;u,v,w)]dx\,dy\,dz\,du\,dv\,dw,$$

where *x,y,z* were spatial coordinates and *u,v,w* velocity coordinates. The integral was extended to a six-dimensional hyper-space, and the minus before the integral transformed the search for the minimum into the search for the maximum. This was the quantity whose value had to be computed "when the gas has reached thermal equilibrium". As already shown, at the equilibrium,

$$f(x,y,z;u,v,w)=\frac{N}{V\left(\frac{4\pi T}{3m}\right)^{3/2}}e^{-\frac{3m}{4T}\left(u^2+v^2+w^2\right)},$$

where V was the volume of the gas, m the mass of every molecule, T the average living force, and N the number of molecules. When we put the function into Ω, the integral yields

$$\Omega=N\log\left[V\left(\frac{4\pi T}{3m}\right)^{3/2}\right]+\frac{3}{2}N-N\ln N.^{22}$$

Apart from the reversed signs and the last constant on the right-hand side, Boltzmann arrived essentially at the expression already found in 1872. At that time, he had briefly stated that it corresponded essentially to "the entropy of a mono-atomic gas". Five years later, he tried to carefully compute the entropy, starting from a particular expression of the first Principle, and the equation of state for perfect gases:

$$dQ=NdT+pdV$$
$$pV=\frac{2}{3}NT.$$

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[22] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 215-6. The general solution of the integral-differential equation for $f(x,t)$ was found in 1916-7. See Brush 1976, book 1, p. 237, and book 2, p. 449.

The computation of entropy required only a simple integration:

$$\int\frac{dQ}{T}=\int N\frac{dT}{T}+\int\frac{pdV}{T}=N\ln T+C_1+\int\frac{2}{3}\frac{NT}{VT}dV=N\ln T+C_1+\frac{2}{3}N\int\frac{dV}{V}$$

$$=N\ln T+C_1+\frac{2}{3}N\ln V+C_2=\frac{2}{3}N\left(\frac{3}{2}\ln T+\ln V\right)+C=\frac{2}{3}N\left(\frac{3}{2}\ln T^{3/2}+\ln V\right)+C$$

$$=\frac{2}{3}N\ln\left(VT^{3/2}\right)+C.$$[23]

Boltzmann stressed the structural similarity between the function Ω, representing the probability of a given state, and the entropy dQ/T in any "reversible change of state". Apart from a constant, the increase of "the measure of permutability multiplied by 2/3" equalled "the increase of entropy".

> Es ist nun bekannt, daß, wenn in einem Systeme von Körpern lauter umkehrbare Veränderungen vor sich gehen, dann die Gesamtsumme der Entropie aller dieser Körper konstant bleibt. Sind dagegen unter den Vorgängen auch nicht umkehrbare, so muß die Gesamtentropie aller Körper notwendig wachsen, wie bekanntlich aus dem Umstande folgt, daß dQ/T über einen nicht umkehrbaren Kreisprozeß integriert, negativ ist. Gemäß der Gleichung (65) muß also auch die Summe der Permutabilitätsmaß aller Körper $\sum\Omega$ oder das gesamte Permutabilitätsmaß derselben zunehmen. Es ist daher das Permutabilitätsmaß eine Größe, welche für den Zustand des Wärmegleichgewichtes bis auf einen konstanten Faktor und Addenden mit der Entropie identisch ist, welche aber auch während des Verlaufes eines nicht umkehrbaren Körpers einen Sinn behält, und auch während eines solchen fortwährend zunimmt.[24]

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[23] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 216. For a comparison with his 1872 line of reasoning, see Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 399-400.

[24] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 217. Cassirer found that Boltzmann had managed to remove the "paradoxical and extraneous nature (Fremdheit)" of the second Principle of Thermodynamics in the context of Mechanics. Just for this reason, he qualified Boltzmann as "one of the most rigorous representatives of classic Mechanics". See Cassirer E. 1936, pp. 95-6. The fact is that, in Boltzmann's theory, the second Principle did not stem from Mechanics, but from statistical and probabilistic hypotheses unrelated to Mechanics. Just for this reason, I find that Boltzmann was not a "classical physicist".

In the last pages of the paper, in many ways Boltzmann emphasised the relationship between the computation of the complexions corresponding to a given physical state, and the computation of the entropy. Although the entropy could not be computed out of "thermal equilibrium", the computation of "the measure of permutability" could be performed in any case. Even in cases wherein "*initial and final state*" were not equilibrium states, the value of permutability in the course of the transformation would "*continuously increase*", or at most could "*maintain a constant value as long as all the bodies are in thermal equilibrium*". He acknowledged the existence of mathematical and physical difficulties: he had not been able to put forward "an exact mathematical implementation" of the theory which included solid and liquid bodies. At that stage, the nature of those "states of aggregation" was far less known than the nature of gases, and physicists could not rely on mathematical models as powerful as the kinetic theory of gases. Nevertheless, he found "probable" that the deep physical meaning of his theoretical model, and the intimate link between distributions of probability and entropy was not confined to gases: his theoretical model could be looked upon as "a general law of nature".[25]

Boltzmann was aware of the originality of his contribution to Thermodynamics; at the same time, he was conscious that his mathematical model represented a simplification and an idealisation. What he did not explicitly discuss was whether he had actually managed to attain a mechanical explanation of the second Principle of Thermodynamics. In some way, he let some people believe he had, and this belief triggered off the subsequent widespread debate on the possibility of a mechanical foundation of the second Principle. What he had really managed to obtain was the derivation of the second Principle from an original and questionable alliance between mechanics and probability.

There is no doubt that Boltzmann opened new perspectives in physics: from the problematic alliance between physics and probability, new interpretations of physical phenomena emerged. In a lecture he gave in 1886, he imagined a body moving in a definite direction with a given velocity as an "infinitely improbable configuration of energy".

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[25] Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 217-8 and 233.

According to that view, "visible motion behaves like heat of infinitely high temperature", which "can be completely transformed into work". In some way, Mechanics became an extreme implementation of thermodynamic laws: this sounds quite astonishing when we see that Boltzmann is sometimes associated to the so-called *mechanical world-view*.[26]

However, in the 1880s, some German-speaking scientists cast doubts on atomism and microscopic interpretations of the second principle of Thermodynamics: among them we find the young Planck, who had an extraordinary tenure at the University of Kiel. In 1882, in the last paragraph of a paper devoted to vaporisation, melting and sublimation, he made some sharp remarks on the second Principle. He found that the consequences of that principle and "the assumption of finite atoms" were mutually "incompatible", and imagined that "a battle (Kampf) between the two hypotheses" would have taken place in the near future. Making use of an emphatic metaphor, which did not fit in with the plain style of the paper, Planck foresaw that the battle would lead to "the loss of life" for one of the opponents. Although he considered "however premature" any definite prediction, he saw some evidence in favour of the hypothesis of "continuous matter" and against the atomic theory, "its great results notwithstanding".[27]

The foundations of Thermodynamics, in particular the conceptual link between Mechanics and Thermodynamics had also attracted Maxwell. In subsequent editions of his *Theory of Heat*, entropy was acknowledged as a fundamental physical entity, which represented "a distinct physical property of the body depending on its actual state", besides volume, pressure, and temperature. In isothermal processes taking place at a temperature ϑ, the heat which enters a body "causes the entropy to increase from ϕ_1 to ϕ_2", and the amount of heat equals

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[26] Boltzmann L. 1886, in Boltzmann L. 1974, p. 22. See also Cassirer E. 1936, pp. 95-6.

[27] Planck M. 1882, pp. 474-5. In a footnote he made reference to two recent German editions of Maxwell's *Theory of Heat*, in particular to a passage where the author played with an omnipotent being who was able to separate fast from slow molecules. See Maxwell J.C. 1872, pp. 308-9, and Maxwell J.C. 1885, pp. 328-9. See Kuhn T.S. 1986, pp. 23-4 for the identification of Planck's reference to German editions with the above mentioned passage by Maxwell.

$\vartheta(\phi_1 - \phi_2)$. If e represents the energy of the physical system, the mechanical work done by the system "during the process cannot, therefore, be greater than" $de - \vartheta \cdot d\phi$. Maxwell acknowledged that, in previous editions of his book, he had identified the entropy with the available energy, "thus introducing great confusion into the language of thermodynamics". In the new edition, he had "endeavoured to use the word Entropy according to the original definition by Clausius": as a consequence, now "the greater the original entropy", the smaller "the available energy of the body" was.[28]

Maxwell also dealt with the relationship between Clausius' entropy and W. Thomson's "dissipation". He noted that, when a quantity H of heat was communicated "from a body at one given temperature, ϑ_1, to another given temperature, ϑ_2", the increase of entropy was

$$H\left(\frac{1}{\vartheta_2} - \frac{1}{\vartheta_1}\right).$$

In the transformation, the total energy remained unchanged, but "the available energy" was "diminished", and this fact corresponded to "what Sir W. Thomson has called the Dissipation of Energy". He specified that the concept of dissipation was "closely connected with" the concept of entropy, even though they were not "identical". According to Maxwell, the energy dissipated "or rendered unavailable as a source of mechanical work" was

$$H\vartheta\left(\frac{1}{\vartheta_2} - \frac{1}{\vartheta_1}\right),$$

where ϑ denoted "the final temperature of the system when it has reached the state of thermal and mechanical equilibrium".[29]

Maxwell saw a sort of symmetry, both physical and mathematical, between mechanical work and heat. It is true that we can distinguish heat from work when they are transferred from a body to another: mechanical work "is done by motion against resistance", whereas

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[28] Maxwell J.C. 1885, pp. 162-3 and 189. The last revised edition was published after Maxwell's death.

[29] Maxwell J.C. 1885, pp. 192-3.

heat “is communicated from a hotter to a colder body”. Nevertheless, “when energy has entered the second body”, we are not able to distinguish “by any legitimate process whether it is in the form of work or of heat”. This seems nothing else but the core of the first Principle of Thermodynamics: both heat and mechanical work communicated to a body can give rise either to mechanical or thermal effects. Moreover, from the mathematical point of view, there was a formal analogy between the performed mechanical work $dW = p \cdot dv$ and the exchanged heat $dQ = \vartheta \cdot d\phi$. If pressure brought about mechanical equilibrium in the case of “its equality in *two communicating* vessels”, and a flow of fluid in the case of “its excess in either”, the temperature brought about thermal equilibrium in the case of “its equality in two bodies in contact”, and to a flow of heat in the case of “its excess in either”.[30]

A widespread debate on the foundations of Thermodynamics involved the scientific community for many years, even though the majority of British physicists were not interested in formal symmetries but in the mechanical and probabilistic interpretations of the second Principle. Edward P. Culverwell was one of the British scientists who were dissatisfied with Boltzmann’s explanation of the drift of a physical system towards equilibrium. In 1890, he had remarked that “no one” had managed to show that “a set of particles having any given initial conditions” would have approached the “permanent configuration” of equilibrium, “as time goes on”.[31]

In 1891, in the already mentioned *Report*, his colleague Bryan remarked that the “dynamical properties” of molecules must “differ in some manner from those of a finite number of particles or rigid bodies”. Just for this reason, he found it impossible “to deduce the Second Law … from purely mechanical principles” unless some “axiomatic assumptions” on the nature “of the molecules whose motion produces the phenomenon of heat” were made.[32]

Bryan stressed the impossibility “to fully solve the problem of an infinite number of bodies”, when we consider that “even the Problem of

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[30] Maxwell J.C. 1885, pp. 194-5.

[31] Culverwell E.P. 1890, p. 95. Among the problems still unsolved, Culverwell mentioned the determination of the mathematical law for intermolecular force, and the role played by the luminiferous aether.

[32] Bryan G.H. 1891, pp 87.

Three Bodies has not been fully solved". Despite this, he did not exclude that it was possible "to investigate certain irreversible phenomena by the methods of the kinetic theory", and therefore "to account for the degradation of available energy", provided that physicists gave up a detailed mechanical analysis. He mentioned the attempt made by Peter G. Tait to compute "the rate of equalisation of average energy in a mixture of two kinds of spheres". Moreover he acknowledged that the kinetic theory had successfully managed to account for phenomena such as "heat conduction, viscosity, diffusion of a mixture of gases" …, which were actually "irreversible processes".[33]

The inescapable contradiction between the time-reversibility of mechanical equations and the time-irreversibility of thermal processes was at stake, and Bryan took into account the virtual possibility that "the motion of every point" was "exactly reversed". Here we are dealing with one instance of the well-known and fruitless discussion on the sudden reversal of molecular velocities, which skipped any consideration on the huge amount of energy and information which would be required to realise that fictional inversion. In any case, Bryan stated that the irreversibility of thermal processes could be justified "on statistical grounds alone", and specified that he was speaking of "a possible explanation, and not a proof, of the principle of degradation of energy". Time-reversibility of mechanical equations was still the most disturbing stumbling block on the pathway to a satisfactory integration between Mechanics and Thermodynamics.[34]

Finally, he reminded the reader how questionable the influence of aether was over thermodynamic processes, even though he ventured to assume that aether "will certainly facilitate the dissipation of energy". If the "highest" aim of the scientific enterprise was to help us to "judge the unknown from the known", then the kinetic theory was not consistent with that "sentiment". In fact, how could we hope to "prove the Second Law, about which we know something", by means

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[33] Bryan G.H. 1891, p. 119.

[34] Bryan G.H. 1891, p. 120. He reported a curious and misleading example: "Although a conservative dynamical system is always reversible, the reversed motion may not infrequently be dynamically instable in the highest degree. One of the best illustrations in point is afforded by the possibility of riding a bicycle backwards (i.e. with the steering wheel behind); here the forward motion is stable, but the reversed motion is highly unstable."

of molecules, “about which we know much less”? Bryan concluded his *Report* with the very general expectation that “future researches” could “further strengthen the bond of connection” which he supposed “to exist between the Second Law of Thermodynamics and Newton’s Laws of Motion”. It was quite an unspecific expectation indeed.[35]

In 1893, Poincaré remarked that Mechanics required that “all phenomena are *reversible*”, even though every experience contrasted that requirement: thermal conduction was a well-known instance of irreversibility. That a scientist could expect thermal irreversibility to stem from the laws of Mechanics, seemed logically inconsistent to Poincaré: how could we rely on a theory wherein “we find reversibility at the outset, and irreversibility at the end”?[36]

In 1894, Boltzmann took part to the annual meeting of the British Association for the Advancement of Science, and his communications raised some debate, which continued in the pages of the scientific journal *Nature* in 1895. In January 1895, Culverwell sent a letter to the journal, where he briefly discussed Larmor, Samuel H. Burbury, Bryan, and Henry W. Watson’s remarks on Boltzmann’s “H-theorem”. He stressed that the proof of the theorem could not be valid unless “some assumption about averages, probability, or irreversibility” was introduced. In other words, what had to be demonstrated had in reality been assumed from the outset. Culverwell demanded “a *proof* that the collisions will make H decrease”, and was not satisfied with “a proof which depends on the previous assumption” that molecules “naturally” collide “in the desired way”.[37]

The British journal also hosted a paper where Boltzmann tried to clarify his probabilistic approach to Thermodynamics. He started

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[35] Bryan G.H. 1891, pp. 120-22.

[36] Poincaré H. 1893, pp. 534-7. In 1896 and 1897 Boltzmann answered systematically to Zermelo and Poincaré’s criticism, and stressed the intrinsic statistical nature of his approach: from his point of view, “Poincaré’s theorem” was “completely in accordance” with his own theorems. In 1896 he remarked that the entity of Poincaré’s recurrence time “makes a mockery of every attempt at observing it”, and in 1897 stressed that “[i]n practice … a numerical upper boundary for the time of recurrence … cannot be specified”. See Boltzmann L. 1896b, in Boltzmann L. 1909, III Band, p. 571, and Boltzmann L. 1897c, in Boltzmann L. 1909, III Band, p. 595. For the debate, see Dugas R. 1959, pp. 207-8 and 212-3, Brush S. 1976, book 1, p. 96, and Brush S. 1976, book 2, pp. 356-63. In 1906 Poincaré returned to the concept of entropy, and put forward two different kinds of entropy. See Cercignani C. 1997, pp. 98-9, 103, and 149.

[37] Culverwell E.P. 1895, p. 246. See Brush S. G. 1976, book 2, p. 622.

from two questions of very general nature: in the first, he asked if "the Theory of Gases" was a good theory, and in the second, "What we demand from any physical theory". He claimed that the second question did not belong "to ordinary physics", but to some meta-theoretical level which he qualified as "orthophysics" or "metaphysics". In reality the two questions shared the same meta-theoretical nature, and the first did not refer to the theory of gases in general, but specifically to the kinetic theory of gases. According to Boltzmann, it was a good theory, and he undertook a historical and conceptual analysis in order to justify the confidence he had claimed.[38]

Boltzmann's historical analysis started from Boscovich's model of force, which he qualified as "the ideal of physicists" because of the pretention to explain "everything". Unfortunately, neither "all the material points of the universe" nor "the law of mutual force for each pair" were exactly known. Nevertheless, the solution could be outlined, at least qualitatively: even though the comprehension of nature was "a difficult problem", it was in no way "a mystery for the human mind". He made explicit reference to the Presidential Address held by Lord Salisbury at Oxford in 1894, in which the speaker had claimed that "nature is a mystery", and that the nature of atoms in particular "was "surrounded by profound darkness".[39]

Boltzmann believed that the kinetic theory could "explain the spectra of gases, while ascribing 5 degrees of freedom to the molecules", in general accordance with "Boscovich's standpoint". He assumed that the molecules "of the gas and of the enclosing vessel" behaved "as rigid bodies" moving through the aether "without loss of energy". In alternative, molecules could be represented as "Lord Kelvin's vortex rings" moving "through a frictionless liquid". He acknowledged that the explanation of the role of aether was really a demanding task: it came "from the universe", flowed "freely through the walls of the vessel", and it was "not at all in thermal equilibrium with the molecules of the gas". When the outer space was colder than the gas, aether carried off energy, but that energy was probably "so small as to be quite negligible" in comparison with "the energy which the gas loses by heat-conduction". He assumed that only transversal aethe-

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[38] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, p. 535.

[39] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, pp. 535-6.

real radiations could "transfer sensible energy from one ponderable body to another": as a consequence, "a correction for radiant heat" was required, in order to account for the value of "specific heats".[40]

Another difficulty of the model stemmed from the mutual compatibility between the mechanical model of simple rigid bodies, and the theoretical necessity of molecules "composed of smaller atoms". He assumed that the *vis viva* of "internal vibrations" of atoms was transformed into "progressive and rotational motion" of molecules, but the transformation was very slow. In particular, he assumed that the molecules might "retain for days, or even for years" the higher *vis viva* "of their internal vibrations corresponding to the original temperature", when the gas was brought to a lower temperature. Even though he avowed that those assumptions were "nothing more than a series of imperfectly proved hypotheses", he was satisfied with the fact that an "explanation" was "not impossible" in general terms.[41]

In the following section, Boltzmann faced the most sensitive issue: the interpretation of the second Law of Thermodynamics. He clearly stated that the second Law could "never be proved mathematically by means of the equations of dynamics alone". This was a very important statement, because he explicitly acknowledged that something else was at stake besides the mechanical model of the kinetic theory. In reality, that *something else* was the statistical independence of the dynamical parameters of the different molecules, and it was a hypothesis in contrast with the laws of mechanics. He reminded the reader that Culverwell had tried "to refute" his "Minimum Theorem" by imagining the sudden reversal of molecular velocities in a gas. If the molecules had followed the laws of mechanics, the value of his function H could not decrease but increase. According to Boltzmann, the solution of the paradox lay outside Mechanics: mechanical equations of motion could not prove that "the minimum function H must always decrease". In some sense Boltzmann's answer to Culverwell's objection was in accordance with Culwerwell's objection itself: the demonstration of Boltzmann's theorem required "some assumption" of non-mechanical nature. That result could "only be deduced by the laws of probability", and he immediately specified that "the theory of

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[40] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, p. 537.

[41] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, pp. 538-9.

probability is as exact as any other mathematical theory", in order to assure the reader that probability did not have to be confused with some kind of qualitative uncertainty. The reversal of velocities could not affect qualitatively the behaviour of the function *H*; after the reversal, the function *H* would inevitably begin to decrease once again.[42]

In reality, Boltzmann's most interesting remark emerged from the last passages of the paper, where he put forward a line of reasoning which he attributed to his "old assistant Dr. Schuetz". The probability that only one part of the universe was "in a certain state", was "the smaller" the further this state was "from thermal equilibrium". At the same time, the probability was greater "the greater the universe itself is". As a consequence, the probability that "such a small part of it as our world should be in its present state" was "no longer small". In other words, our "world", which was assumed to be only an infinitesimal fraction of the universe, was imagined as an unpredictable fluctuation. More in general, Boltzmann assumed that his *H*-curve "would form a representation of what take place in the universe" as a whole. Because of its extreme extension, he could not exclude that, "at some future time", some other world "might deviate as far from thermal equilibrium as our world does at present". Those worlds would be placed in the higher regions of the curve, which would correspond to "worlds where visible motions and life exist".[43]

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[42] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, pp. 539-40. See Culverwell E.P. 1895, p. 246 (above quoted). There was another issue, indeed, which Boltzmann did not face explicitly, a fundamental question which emerges whenever the controversy about the reversal of velocities comes into play: where would the required energy come from?

[43] Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, pp. 543-4.

4. ON THE SECOND PATHWAY: THE THEORETICAL PHYSICS OF ENGINEERS

In the second half of the nineteenth century, a different 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 1851 a short paper of Ferdinand Reech appeared in the *Comptes Rendus de l'Académie des Sciences*, in the section *Mathématiques Appliquées*. He was a Naval engineer and director of the *École du Génie Maritime*. He reminded the reader of the content of Carnot's 1924 essay, which he synthesises in the mathematical law

$$S = q\left[\Gamma(t') - \Gamma(t)\right],$$

where S was "the quantity of motive force", q "the quantity of caloric" exchanged between two "sources of heat", and $\Gamma(t)$ a universal function of temperature. According to Carnot and to Clapeyron's subsequent interpretation, Reech stated that the motive force generated by thermal engines stemmed from the transfer of that amount q of heat from a source A' at the temperature t' to a source A at a lower temperature t. He remarked that the transfer of caloric could not be transformed into mechanical force completely, because "friction and passive resistance" could not be disregarded: moreover, the caloric "sent out by the chimney" and "the thermometric fall" in the condenser had to be taken into account too.

Both the existence of caloric dissipation and the probable inequality between the amount of caloric q' received by A' and the amount q sent to A, as shown experimentally by Regnault, led Reech to assume a more general relationship between motive force, caloric and temperature:

$$S = q'\Gamma(t') - q\Gamma(t) = q'\Gamma(t') - q\Gamma(t') + q\Gamma(t') - q\Gamma(t) = \\ = (q' - q)\Gamma(t') + q\left[\Gamma(t') - \Gamma(t)\right].$$[1]

He resumed the subject in a long essay he published in the *Journal de Mathématiques pures et appliquées* in 1853, and reprinted as a separate volume *Théorie générale des effets dynamiques de la chaleur* the following year. He mentioned Joule, Thompson [sic], Rankine, Mayer and Clausius' recent researches, and regretted that "mere hypotheses were given so great importance": he claimed that "the logic consistency of the reasoning" should have been restored. The "new point of view", which he developed in that volume, was subsequently summarised in a paper published in the same mathematical journal in 1856. In the latter he stressed the "algebraic" character of his inquiry, which was very general and consistent with different physical hypotheses. He pursued a very demanding task: he aimed at deriving nothing less than the most general and complete amount of "formulae" consistent with "the totality of future experiments" undertaken by physicists.[2]

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[1] Reech F. 1851, pp. 567-8 and 570. The role of Reech was emphasised by Ambrose C. Truesdell: he defined the textbook Reech published in 1868 as "the clearest presentation of the subject I have ever seen" (Truesdell A.C. 1980, p. 299). See also Truesdell A.C. 1980, chapter 10, where Truesdell rephrased Reech's theories in modern terms. See also Truesdell C. and Bharatha S. 1977, chapters 8 and 14.

[2] Reech F. 1854, p. 1, and Reech F. 1856, p. 61. In a footnote he stressed the mathematical character of his researches: "Mon but n'a jamais étè de m'occuper de ces matières comme

His theory was quite a mathematical one indeed. He started from the previous equation, which he re-wrote in an integral form,

$$S = q'\Gamma(t') - q\Gamma(t) = \int_{t}^{t'} \frac{d\left[q\Gamma(t)\right]}{dt} dt.$$

The function $\Gamma(t)$ was the same "for all bodies in nature", and from this general mathematical framework he could briefly discuss the recently re-emerged kinetic theory of heat. Since "heat would be equivalent to the living force", in this case S and q would have the same physical dimension: therefore the function $\Gamma(t)$ had to be a constant quantity. Then he analysed Fourier's theory of heat conduction, wherein "there is neither production of work nor any kind of waste", and therefore $q' = q$ and $S = 0$. As a consequence, $q'\Gamma(t') = q\Gamma(t)$, and $\Gamma(t') = \Gamma(t) = const$ as well. In conclusion, he noted that "at present it is widely accepted" that

$$S = G\left(q' - q\right).^{3}$$

The attempt to integrate the different traditions of the science of heat, namely the Fourier flow of heat without mechanical work, the Carnot transformation of heat into mechanical work without free flow of heat, and the Joule equivalence between heat and mechanical work, led Reech to generalize the mathematical interpretation of Carnot's cycle. Provided that the internal surface of the closed line representing the cycle in a plane (v,p) corresponded to S, he assumed that the isothermal transformations were expressed by the equations $\varphi(v,p) = t$, $\varphi(v,p) = t'$, and the adiabatic ones by $\psi(v,p) = u$, $\psi(v,p) = u'$. To the amount of heat q and q' he associated the very general functions

$$q = \int_{u}^{u'} f(t,u)du, \quad q' = \int_{u}^{u'} f(t',u)du,$$

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physicien, mais seulement comme logicien, particulièrement en ce qui concerne le perfectionnement de la théorie des machines motrices, …" (Reech F. 1856, pp. 65-6)

[3] Reech F. 1856, pp. 59-60.

which could be simplified when taking into account experimental data concerning "some physical properties of vapours":

$$q = \int_{u}^{u'} \gamma(t) du = \gamma(t)(u' - u), \quad q' = \int_{u}^{u'} \gamma(t') du = \gamma(t')(u' - u).$$

As a consequence, what Reech called "Causius' second theorem" followed:

$$\frac{q'}{\gamma(t')} = \frac{q}{\gamma(t)}.$$

He had already tried to demonstrate that "the amount of work which can be generated by the totality of heat contained in an elastic fluid" was "an exact differential". Unfortunately, Clausius' second theorem and the existence of such an exact differential were not mutually consistent: Reech and Clausius' perspective could not but diverge.[4]

After thirteen years, another 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 pdv was "thermally equivalent" to $Apdv$, wherein A was the well-known conversion factor between mechanical and thermal measures. The first principle could therefore be expressed by the equation

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[4] Reech F. 1856, pp. 60-1and 65.

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

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".[5]

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 ψ whose differential

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

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

$$U = T^2 \frac{\partial\psi}{\partial t} \text{ and } S = \psi + T\frac{\partial\psi}{\partial t}, \text{ or } S = \frac{\partial}{\partial t}(T\,\psi) \text{ and } \psi = S - \frac{U}{T}.^{6}$$

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

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

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[5] Massieu F. 1869a, p. 858.

[6] Massieu F. 1869a, p. 859, and Massieu F. 1869b, p. 1058. In the first paper, Massieu did not distinguish partial from total derivatives.

In the case of ideal gases,

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

and ψ and ψ' resulted the same function, apart from a constant value.[7]

Massieu claimed that not only could U, p, v, Q and S be derived from ψ and ψ', but also the specific heats at constant pressure or volume k and k', and the coefficient of dilatation at constant pressure or volume β and β' could as well. Conversely he was able to give the specific mathematical expressions of ψ and ψ' in terms of T, v, p, and the specific heats k and k', for ideal gases, saturated vapours and superheated vapours.[8]

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 unifying power of Thermodynamics, which he identified with "the mechanical theory of heat".[9]

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

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[7] Massieu F. 1869b, pp. 1059-60.

[8] Massieu F. 1869b, pp. 1060-1.

[9] 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."

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 diverses fluides.[10]

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".[11]

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

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

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[10] Massieu F. 1876, pp. 2-3.

[11] Massieu F. 1876, pp. 3-8.

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

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

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

$$S = \frac{dH}{dt}, \; Ap = \frac{dH}{dv}, \; U = ST - H \text{ or } U = T\frac{dH}{dt} - H.^{12}$$

An important feature of ideal gases could be derived from the mathematical properties of the characteristic function, because their internal energy did nor depend on volume but only on temperature. Expressions for k, k', β, β', 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.[13]

The choice of t and p instead of t and v as independent variables led to Massieu's second characteristic function H', which corresponded to the function ψ' of the previous paper. A two-fold strategy, both mathematical and physical, was at stake. On 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.[14]

On the other hand, all parameters and specific equations describing the specific system could be derived from the knowledge of H': in

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[12] Massieu F. 1876, pp. 9-10.

[13] Massieu F. 1876, pp. 10-25.

[14] Massieu F. 1876, p. 29.

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.[15]

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, 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.[16]

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.[17] 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",

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[15] Massieu F. 1876, p. 43.

[16] 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."

[17] Rankine had just been appointed to the chair of civil engineering in Glasgow, and he had been Fellow of the *Royal Society* since 1853.

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.[18]

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 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

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[18] Rankine M. 1855, in Rankine M. 1881, pp. 213-4.

> the means of deducing the laws of one class of objects or phenomena from those of another.[19]

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".[20]

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.

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[19] Rankine M. 1855, in Rankine M. 1881, p. 210.

[20] 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 book). Rankine's choice of labelling "*objective*" and "*subjective*" the two interpretations of the "hypothetical method" appears quite misleading.

> 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.[21]

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 "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".[22]

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

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[21] Rankine M. 1855, in Rankine M. 1881, p. 211.

[22] See Rankin 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."

solid" were complex accidents for they required more than one independent variable (accident) to be specified.[23]

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
>
> $$\left.\begin{array}{l} W = \int_{x_0}^{x_1} X\,dx, \quad and \\ W = X(x_1 - x_0), \quad if\ X\ is\ const. \end{array}\right\}.$$
>
> Work is represented geometrically by the area of a curve, whereof the abscissa represents the passive accident, and the ordinate, the effort.[24]

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:

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

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[23] Rankine M. 1855, in Rankine M. 1881, pp. 214-6.

[24] Rankine M. 1855, in Rankine M. 1881, pp. 216-7.

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

$$W = X\,dx + Y\,dy + Z\,dz + \ldots\ldots$$[25]

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.[26]

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.

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[25] Rankine M. 1855, in Rankine M. 1881, pp. 217 and 222.

[26] 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.

> … 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 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.[27]

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".[28]

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.[29] In the two papers, Rankine started from a thermodynamic system formed by an unspecified substance "occupying the bulk V under the pressure P, and possessing the absolute quantity of thermometric heat whose mechanical equivalent is Q". The substance could experience "the indefinitely small increase of

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[27] Rankine M. 1855, in Rankine M. 1881, p. 218.

[28] Rankine traced back the cosmological implication of the theoretical argument to Newton' *Principia*, in particular the "Scolium to the Laws of Motion". See Rankine M. 1855, in Rankine M. 1881, p. 218.

[29] 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".

volume dV". He investigated the process when "the thermometric heat" of the substance was maintained constant by the supply of heat from an external source: here we are dealing with an isothermal transformation. He inquired into the transformations of heat, in particular "how much heat becomes latent, or is converted into expansive power". 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.[30]

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. For the whole "mechanical power" he chose the expression

$$Q \cdot \frac{dP}{dQ} dV.$$

This amount of energy had to be imagined as composed of two parts: the macroscopic, visible work performed by the substance, and the microscopic, invisible work "expended in overcoming molecular attraction". The latter was therefore expressed by

$$Q \cdot \frac{dP}{dQ} dV - P\,dV = \left(Q \cdot \frac{dP}{dQ} - P \right) dV.$$

Rankine remarked that molecular attraction could be derived from a potential S, which was a function of V and Q. In this case, the above equation became

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[30] Rankine M. 1853a, in Rankine M. 1881, p. 311, 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.

$$dS(V) = \left(Q \cdot \frac{dP}{dQ} - P \right) dV \quad \text{or} \quad \frac{\partial S}{\partial V} = Q \cdot \frac{dP}{dQ} - P.$$[31]

In the framework of Rankine's thermodynamics, the whole heat "which is consumed" would correspond to the flux of heat coming from outside. It consisted of the sum of two terms: sensible heat and latent heat. In its turn, the latter could be split into two terms: the fraction of latent heat "which disappears in overcoming molecular action", and the fraction "equivalent to the visible mechanical effect". Not only could this sum be split into sensible and latent heat, but also into internal heat and work, on the one hand, and external work, on the other. The first component, which Rankine had labelled Ψ in a previous paper, was "the sum of the heat of the body and of the potential of its molecular actions". This function would correspond to "the total amount of power which must be exercised on a body", both in the form of heat or mechanical power, "to make it pass from a given volume and temperature to another". In other words, it was a state function.[32]

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 applications, Rankine remarked that the thermal engine with the best efficiency had to correspond to a cycle operating by means of two isothermal and two adiabatic transformations, just like Carnot's model.[33]

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.

> Let Q denote the quantity of a form of actual physical energy present in a given body;

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[31] Rankine M. 1853a, in Rankine M. 1881, pp. 312-3.

[32] Rankine M. 1853a, in Rankine M. 1881, pp. 313 and 317, and Rankine M. 1853b, in Rankine M. 1881, pp. 206-7.

[33] Rankine M. 1853a, in Rankine M. 1881, p. 315.

> V, a measurable state, condition, or mode of existence of the body, whose tendency to increase is represented by
>
> P, a force, depending on the condition V, the energy Q, and permanent properties of the body, so that
>
> PdV is the increment of a form of potential energy, corresponding to a small increment dV of the condition V.
>
> Let dS be the quantity whereby the increment of potential energy PdV falls short of the quantity of actual energy of the form Q, which is converted into the potential form by the change of condition dV.
>
> Then …
>
> $$\frac{\partial S}{\partial V} = Q \times \frac{dP}{dQ} - P$$
>
> an equation from which all those in the previous articles are deducible, and which comprehends the whole theory of the mutual conversion of the actual form of energy Q, and the potential form $\int PdV$, whatsoever those forms may be, when no other form of energy interferes.[34]

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. If the first process led to the concept of "METAMORPHIC FUNCTION", the second led to the concept of "METABATIC FUNCTION".

With regard to the first process, Rankine defined "*the rate of transformation*" of actual energy into work in case of any accident x and its corresponding effort X:

$$dH = Q\frac{dX}{dQ}dx = Q\frac{d^2W}{dQdx}dx = Qd\left(\frac{dW}{dQ}\right).$$

In general, when the work W depended on many forces X, Y, Z, …

$$dH = Q\left(\frac{dX}{dQ}dx + \frac{dY}{dQ}dy + \frac{dZ}{dQ}dz + \dots\right) = Qd\left(\frac{dW}{dQ}\right).$$

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[34] Rankine M. 1853a, in Rankine M. 1881, p. 318.

The function $dF = d(dW/dQ)$ or $F = dW/dQ$ was labelled "METAMORPHIC FUNCTION" by Rankine: it corresponded to the fraction of actual energy transformed into work. The function H corresponded to the amount of actual energy transformed into work.[35]

With regard to the second process, Rankine tried to mathematically generalise heat exchange. He associated an effort X of unspecified nature to the "tendency of one substance to transfer actual energy of the kind Q to another", and re-introduced the fraction of effort "caused by that actual energy" $Q(dX/dQ)$. Then he wrote down the conditions of equilibrium; at the end of the actual energy transfer,

$$X_A = X_B \quad \text{and} \quad Q_A \frac{dX_A}{dQ_A} = Q_B \frac{dX_B}{dQ_B}.$$

As a consequence, $dQ_A / Q_A = dQ_B / Q_B$, and the subsequent integration yielded

$$\log(Q_A) - \log(Q_{A_0}) = \log(Q_B) - \log(Q_{B_0}),$$
$$\log(Q_A) - \log(Q_B) = \log(Q_{A_0}) - \log(Q_{B_0}),$$
$$\log\left(\frac{Q_A}{Q_B}\right) = \log\left(\frac{Q_{A_0}}{Q_{B_0}}\right), \quad \frac{Q_A}{Q_B} = \frac{Q_{A_0}}{Q_{B_0}} = \frac{K_A}{K_B}, \quad \frac{Q_A}{K_A} = \frac{Q_B}{K_B} = \vartheta.$$

The constants K_A and K_B were looked upon by Rankine as the generalisation of specific heats: he named them "SPECIFIC ACTUAL ENERGIES" of A and B. The constant θ, which expressed "the condition of equilibrium of the actual energy Q between them", was labelled "METABATIC FUNCTION", and was looked upon as a generalisation of the concept of "*absolute temperature*".[36]

The physical processes leading to metamorphic and metabatic functions were the generalisation of two different kinds of 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

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[35] Rankine M. 1855, in Rankine M. 1881, pp. 220-2.

[36] Rankine M. 1855, in Rankine M. 1881, pp. 223-5.

sections of the theory of heat which W. Thomson had tried to unify under the concept of "dissipation". Rankine undertook another pathway: a unified mathematical approach for both processes.

Metabatic and metamorphic functions allowed Rankine to reinterpret the operation of engines in general, on the track of Carnot's idealisation of thermal engines.

> In a perfect engine the cycle of variations is thus:
>
> I. The metabatic function is increased, say from θ_0 to θ_1,
> II. The metamorphic function is increased by an amount $\Delta\phi$,
> III. The metabatic function is diminished from θ_1 back to θ_0,
> IV. The metamorphic function is diminished by the amount $\Delta\phi$.
>
> During the second operation, the energy received by the working substance, and transformed from the actual to the potential form is $\theta_1 \Delta\phi$. During the fourth operation energy is transformed back, to the amount $\theta_0 \Delta\phi$. So that the energy permanently transformed during each cycle is $(\theta_1 - \theta_0)\Delta\phi$, and the efficiency of the engine $(\theta_1 - \theta_0)/\theta_1$.[37]

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, "until the value of the *metabatic function* becomes uniform".

> Hence arises the impossibility of using the energy reconverted to the actual form at the lower limit of the metabatic function in an engine.
>
> 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.[38]

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[37] Rankine M. 1855, in Rankine M. 1881, p. 226. Rankine qualified an engine in general as "a contrivance for transforming energy, by means of the periodical repetition of a cycle of variations of the accidents of a substance". Then he qualified the "efficiency" of an engine in general as "the proportion which the energy permanently transformed to a useful form by it, bears to the whole energy communicated to the working substance".

[38] Rankine M. 1855, in Rankine M. 1881, p. 227.

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".[39]

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[39] Rankine M. 1855, in Rankine M. 1881, pp. 227-8.

5. FURTHER DEVELOPMENTS ALONG THE SECOND PATHWAY

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": 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".[1]

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

> I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative. … the condition of equilibrium may be written
>
> $$(\delta\eta)_\varepsilon \leq 0 \quad (1)$$
>
> 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
>
> $$(\delta\varepsilon)_\eta \geq 0 \quad (2)$$[2]

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.[3]

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, … S_n of which

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[1] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 55-6.

[2] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 56.

[3] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 62.

the mass is composed" change their mass. As a consequence, the energy ε of the homogeneous component of the system could also depend on the corresponding variable masses $m_1, m_2, \dots m_n$:

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

where $\mu_1, \mu_2, \dots \mu_n$ denoted "the differential coefficients of ε 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 μ_x Gibbs attributed the qualification of "potential for the substance S_x".[4]

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) ν, wherein ν 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 (ν-1)(n+2) conditions among the (n+2) ν 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".[5] 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 Σ_a, Σ_b, Σ_k … denoted the units of certain substances S_a, S_b, S_k … 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:

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[4] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 63-5.

[5] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 66.

$$\alpha\Sigma_a + \beta\Sigma_b + etc. = \kappa\Sigma_k + \lambda\Sigma_l + etc.$$[6]

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 ψ, χ, and ζ assumed specific meanings, and led to new conditions of equilibrium.

> The quantity ψ has been defined for any homogeneous mass by the equation
>
> $$\psi = \varepsilon - t\eta.$$
>
> 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
>
> $$-d\psi = dW.$$[7]

The function ψ 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

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[6] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 67-9.

[7] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 89.

temperature in the initial and final states, the function ψ played the role of the internal energy ε, and the condition of equilibrium became

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

Gibbs showed that the function ζ 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 χ 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 χ could be qualified as "the *heat function for constant pressure*", and its decrease represents "the heat given out by the system". The system underwent a purely thermal transformation, and in this case Gibbs also stressed the analogy with the internal energy ε, which "might be called the heat function for constant volume".[8]

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. This generalisation led Gibbs to widen the scope of the concept of "potential". Every term μ_1, μ_2, … μ_n, among "the differential coefficients of ε taken with respect to m_1, m_2, … m_n". was qualified by Gibbs as "potential for that substance in the mass considered". As he had already shown some pages before, the potentials μ_i assumed the same differential structure, independently of the choice of the fundamental function:

$$\mu_1 = \left(\frac{d\varepsilon}{dm_1}\right)_{\eta,v,m} = \left(\frac{d\psi}{dm_1}\right)_{t,v,m} = \left(\frac{d\chi}{dm_1}\right)_{\eta,p,m} = \left(\frac{d\zeta}{dm_1}\right)_{t,p,m}$$

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[8] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89-91.

The subscript letters denoted the quantities which remained constant in the differentiation, "*m* being written for brevity for all the letters $m_1, m_2, \ldots m_n$, except the one occurring in the denominator". In this way, the fundamental functions ε, ψ, χ, and ζ were interchangeable: ε as a function of volume and entropy could be replaced by ψ as a function of temperature and volume, by χ as a function of entropy and pressure, or by ζ as a function of temperature and pressure. In brief, every fundamental function, associated to its two independent variables, defined a threefold system of co-ordinates, wherein the graph of the corresponding function $z = f(x,y)$ could be drawn: four functions $\varepsilon = f_\varepsilon(v,\eta)$, $\psi = f_\psi(v,t)$, $\chi = f_\chi(p,\eta)$, and $\zeta = f_\zeta(p,t)$ could be defined. We have in front of us a sort of symmetry, which transforms the space (v,η,ε) into the space (v,t,ψ), (p,η,χ), or (t,p,ζ).[9]

In the section "The Conditions of Internal and External Equilibrium for Solids in Contact with Fluids with regard to all possible States of Strain of the Solids", Gibbs dealt with solids in "*state of strain*", and tried to deduce some mechanical properties from his fundamental equations. The task required more than thirty pages of heavy mathematics, wherein he made use of the fundamental equations involving ε and ψ, as well as "the differential coefficients" $\frac{dx}{dx'}, \frac{dx}{dy'}, \ldots\ldots \frac{dz}{dz'}$ connecting "the *strained* and the *unstrained* states" of the solid. After some approximation, he managed to reach some mathematical expression for "the elasticity of volume and the rigidity", under two different conditions: constant temperature or constant entropy.[10]

Gibbs did not inquire into the molecular structure of matter, even though he briefly mentioned molecules in the first lines of the short section "On Certain Points relating to the Molecular Constitution of

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[9] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89, 93, and 116. See, in particular p. 93: "In the above definition we may evidently substitute for entropy, volume, and energy, respectively, either temperature, volume, and the function ψ; or entropy, pressure, and the function χ; or temperature, pressure, and the function ζ."

[10] See Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 184-5 and 209-14. I will not try to reconstruct the whole deduction, but will confine myself only to stress Gibbs' commitment to a unified mechanic-thermodynamic approach to physical phenomena.

Bodies". He started from the distinction between "proximate components" and "ultimate components" in any physical system. For instance, in "a mixture at ordinary temperatures of vapor of water and free oxygen and hydrogen", we have three "sorts of molecules", namely hydrogen, oxygen and water, and therefore three kinds of proximate components. At the same time, we know that water can be reduced to the ultimate components hydrogen and oxygen: in this case, the number of proximate components "exceeds" the number of ultimate components. Molecules, proximate components and ultimate components shared the same nature of subsets in a complex system: Gibbs assumed neither conceptual differences among them, nor any intrinsic difference between macroscopic and microscopic level. He did not see descriptions in terms of "components" as qualitatively different from descriptions in terms of "molecules": they were "essentially the same in principle".[11]

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

The same view was confirmed in a subsequent abstract Gibbs published in the *American Journal of Science* in 1878. From the outset he stressed the role of entropy, whose importance did "not appear to have been duly appreciated": he claimed that "the general increase of entropy … in an isolated material system" would "naturally" suggest that the maximum of entropy be identified with "a state of equilibrium". He emphasised the role of the function ψ besides the functions ε and η, and the corresponding condition of equilibrium: when "the temperature of the system is uniform", the condition of equilibrium could "be expressed by the formula" $(\delta\psi)_t \geq 0$. 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 generali-

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[11] Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 138.

sation 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".[12]

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 *Gleichgewichtzustände 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 "not necessary". In accordance with this theoretical option, he assumed that isotropic bodies consisted of "*continuous* matter".[13]

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[12] 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."

[13] 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 McCormmach R. and Jungnickel C. 1986, vol. 2, pp. 51-2, 152, and 254, and Gillispie C.C. (ed.), Volume XI, p. 8.

Two years later, in the paper "Verdampfen, Schmelzen und Sublimiren", 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.[14]

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,

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[14] 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. See chapter 8 of the present book.

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".[15]

From the outset he put forward a unified theoretical approach for physical and chemical processes, based on the two principles of Thermodynamics. In particular, he found that thermo-chemical processes, in particular the production or dissolutions of chemical compounds, could not be interpreted in terms of mere production or consumption of heat. A more satisfactory theory had to take into account the fact that an amount of heat was not indefinitely convertible into an equivalent amount of work, according to Clausius' 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.[16]

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[15] 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.

[16] 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.

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.

> Die Berechnung der freien Energie lässt sich der Regel nach nur bei solchen Veränderungen ausführen, die im Sinne der thermodynamischen Betrachtungen vollkommen reversibel sind. Dies ist der Fall bei vielen Lösungen und Mischungen, die innerhalb gewisser Grenzen nach beliebigen Verhältnissen hergestellt werden können. [...] Für die nach festen Aequivalenten geschlossenen chemischen Verbindungen im engeren Sinne dagegen bilden die elektrolytischen Processe zwischen unpolarisirten Elektroden einen wichtigen Fall reversibler Vorgänge. In der That bin ich selbst durch die Frage nach dem Zusammenhange zwischen der elektromotorischen Kraft solcher Ketten und den chemischen Veränderungen, die in ihnen vorgehen, zu dem hier zu entwickelnden Begriffe der freien chemischen Energie geführt worden.[17]

The galvanic cell was indeed the device Helmholtz tried to describe in thermodynamic terms. In processes taking place at constant temperature, the combination of the two Principles of Thermodynamics allowed Helmholtz to compute the balance between electric and thermal contributions. In particular he computed the mechanical equivalent of heat which had to be supplied to the galvanic cell, dur-

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[17] Helmholtz 1882, p. 960.

ing the passage of an "electric quantum" $d\varepsilon$, "in order to keep constant the temperature".[18]

After a very detailed analysis of experimental hindrances involving the complex interplay between electromotive force and dilution, Helmholtz undertook "a theoretical discussion" regarding "a preliminary general analysis of the principles of thermodynamics". He arrived at Thermodynamics after a short detour through the "great simplification and generality" reached by Analytical Mechanics or "Dynamics". He focused on a key concept, which could be labelled "potential energy", "function of force" (*Kräftefunction*), "tension force" (*Quantität der Spannkräfte*), or "Ergal", and which he associated with the names of Clausius, C.G. Jacobi, and himself. In the first applications of this concept, "variations of temperature had not been taken into account", because forces and corresponding works did not depend on temperature, as in the case of gravitation. Nevertheless, "some constant physical entities" appearing in the "Ergal", like density and coefficients of elasticity, "really changed with temperature": a correct and complete mathematical procedure had to start "from the two equations of thermodynamics put forward by Clausius".[19]

Helmholtz labelled ϑ the absolute temperature, and p_α the parameters defining the state of the body: they depended neither on each other nor on temperature. If Clausius had introduced "two functions of temperature and another parameter, which he called the Energy U and the Entropy S", Helmholtz showed that "both of them can be expressed as differential quotients of a completely defined Ergal" or thermodynamic potential. If P_α was the external force corresponding to the parameter p_α, and $P_\alpha \cdot dp_\alpha$ the corresponding work, then the total external work was $dW = \sum_\alpha (P_\alpha \cdot dp_\alpha)$. According to the first principle,

$$\mathrm{J} \cdot dQ = dU + \sum_\alpha (P_\alpha \cdot dp_\alpha),$$

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

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[18] Helmholtz 1882, pp. 961-2.

[19] Helmholtz 1882, pp. 965-6.

> Hierin bezeichnet J das mechanische Aequivalent der Wärmeeinheit und $P_\alpha \cdot dp_\alpha$ die ganze bei der Aenderung dp_α 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.[20]

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

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

Then he derived an equivalent expression from the first Principle:

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

and the physical equivalence led to the mathematical relations

$$\mathrm{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \mathrm{J} \cdot \frac{\partial S}{\partial p_\alpha} = \frac{1}{\vartheta} \cdot \left(\frac{\partial U}{\partial p_\alpha} + P_\alpha \right).$$ [21]

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

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

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

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

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

[21] Helmholtz 1882, p. 967.

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

$$\frac{\partial \mathrm{F}}{\partial \vartheta} = -\mathrm{J} \cdot S, \quad \text{and} \quad U = \mathrm{F} + \mathrm{J} \cdot \vartheta \cdot S \quad \text{or} \quad U = \mathrm{F} - \vartheta \cdot \frac{\partial \mathrm{F}}{\partial \vartheta}.$$[22]

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

> Die Grösse
> $$U = \mathrm{F} - \vartheta \cdot \frac{\partial \mathrm{F}}{\partial \vartheta} = \mathrm{F} + \mathrm{J} \cdot \vartheta \cdot S$$
> könnte, wie bisher, als die gesammte (innere) Energie bezeichnet werden; die etwa vorhandene lebendige Kraft der Massen des Systems bleibt von F wie von U ausgeschlossen, so weit sie zu den frei verwandelbaren Arbeitsäquivalenten gehört, und nicht zu Wärme geworden ist. Dann könnte man die Grösse:
> $$U - \mathrm{F} = -\vartheta \cdot \frac{\partial \mathrm{F}}{\partial \vartheta} = \mathrm{J} \cdot \vartheta \cdot S$$
> als die gebundene Energie bezeichnen.
> Vergleicht man den Werth der gebundene Energie:
> $U - \mathrm{F} = \mathrm{J} \cdot \vartheta \cdot S$,
> mit der Gleichung ...:
> $dQ = \vartheta \cdot dS$;
> so ergiebt sich, dass die gebundenen Energie das mechanische Aequivalent derjenigen Wärmemenge darstellt, die bei der Temperatur ϑ in den Körper eingeführt werden müsste, um der Werth S seiner Entropie hervorzubringen.[23]

According to Helmholtz, another term, namely the living force ("actuelle Energie"), had to appear in the list of energies. This term corre-

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[22] Helmholtz 1882, pp. 968-9. As I have shown in the previous chapter, 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.

[23] Helmholtz 1882, p. 971.

sponded specifically to “the living force of the ordered motion”, and was not to be confused with “the work-equivalent of heat”, which could be considered as the “living force of hidden molecular motions”. The distinction between ordered and disordered motions appeared to Helmholtz as not easy from the mechanical point of view. Only some “good reasons” had led him to assume that thermal motion was of the disordered kind, and that entropy was “a measure of disorder”.[24]

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

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

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

$$dW = \sum (P_\alpha \cdot dp_\alpha) = \sum \left(-\frac{\partial F}{\partial p} \cdot dp_\alpha \right) = -\delta F$$ [25]

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

$$J \cdot dQ = dU - \delta F \;.$$

The free energy represented only a part of the total energy U: the remaining part was labelled “bound energy” or “bound work” or G.

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[24] Helmholtz 1882, pp. 971-2, footnote included. The transformations of energy which took place in “living tissues” appeared to Helmholtz even more difficult to tackle. We can imagine that thermodynamic processes in the human body were of particular interest for a scientist who had begun his career as a physiologist.

[25] Helmholtz 1882, pp. 972-3.

From the mathematical point of view, $\mathrm{F} + \mathrm{G} = U$. Helmholtz offered a mathematical and conceptual alternative to the first principle expressed in terms of *W* and *Q*: $\mathrm{F} + \mathrm{G} = U$ instead of $\mathrm{J} \cdot dQ = dU + dW$.

If $\mathrm{F} = U - \mathrm{J} \cdot \vartheta \cdot S$, then $U = \mathrm{F} + \mathrm{J} \cdot \vartheta \cdot S$ and therefore $\mathrm{G} = \mathrm{J} \cdot \vartheta \cdot S$. The variation of F and G separately yielded

$$d\mathrm{G} = \mathrm{J} \cdot \vartheta \cdot dS + \mathrm{J} \cdot S \cdot d\vartheta = \mathrm{J} \cdot dQ + \mathrm{J} \cdot S \cdot d\vartheta,$$

$$d\mathrm{F} = \delta\mathrm{F} + \frac{\partial \mathrm{F}}{\partial \vartheta} \cdot d\vartheta = -dW - \mathrm{J} \cdot S \cdot d\vartheta.$$

If G grew "at the expense of the entering heat *dQ*", and "at the expense of the free energy" (by $\mathrm{J} \cdot S \cdot d\vartheta$), when the temperature rose, the free energy decreased because of the increase in temperature $\mathrm{J} \cdot S \cdot d\vartheta$, and the increase of the performed external work.[26]

In the specific case of adiabatic transformations, *dQ* = *0*, and therefore $d\mathrm{G} = \mathrm{J} \cdot S \cdot d\vartheta$. The last equation became $d\mathrm{F} = -dW - d\mathrm{G}$ or $dW = -d\mathrm{F} - d\mathrm{G}$, leading Helmholtz to conclude that, in this case, "work is produced at the expense of both free and bound energy". In the specific case of isothermal transformations, $d\vartheta = 0$, and the last two equations became $dW = -d\mathrm{F}$ and $d\mathrm{G} = \mathrm{J} \cdot dQ$. In this case, as Helmholtz stated, "work is performed at the expense of the free energy", and "bound energy changes at the expense of the entering or leaving heat".[27]

In the last short section of the paper, he briefly discussed "the conditions of equilibrium" and "the direction of spontaneous transformations". The quantity $\delta\mathrm{F}$ was independent of temperature, and he stated that "any positive value of $\delta\mathrm{F}$, increasing with time, cannot occur", provided that "any access to reversible external work" could not occur as well. This was the case of chemical phenomena like "dis-

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[26] Helmholtz 1882, pp. 972-3 and 975.

[27] Helmholtz 1882, p. 975. Even though A.F. Horstmann and Gibbs had already acknowledged the role of entropy in chemical processes, Helmholtz's theoretical reinterpretation of the first Principle of Thermodynamics can be looked upon as an important stage in the reshaping of chemical thermodynamics, In France, the influential chemist M. Berthelot went on with the old Thermo-Chemistry. See Kragh H. 1993, pp. 417-8, and 423.

sociation of chemical bonds". Only if δF began to pass "from a nil to a negative value", the phenomenon of dissociation "would take place".[28]

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.[29]

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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[28] Helmholtz 1882, pp. 976-8.

[29] 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.

PART II

Duhem’s Third Pathway

6. 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.[1]

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

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[1] 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.

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.[2]

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 ψ, which in its turn was proportional to Messieu's "fonction caractéristique" H: $F = E(U-TS) = \psi = -EH$.[3]

Duhem wrote the first principle of Thermodynamics as

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

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

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[2] 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.

[3] 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 $EA = 1$.

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,

$$\int \frac{dQ}{T} > 0 \quad \text{namely} \quad \int_0^1 \frac{dQ}{T} + \underset{(r)}{\int_1^0} \frac{dQ}{T} > 0 .$$

Making use of the definition of entropy $\underset{(r)}{\int_1^0} \frac{dQ}{T} = S_1 - S_2$, 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 τ could be interpreted as "an amount of work which can be naturally qualified as *non-compensated work*".[4]

These concepts emphasised the formal analogy between Mechanics and Thermodynamics.

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

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[4] 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".

> *Si une modification isothermique correspond à un travail non compensé positif, elle est possible, mais non réversible.*
>
> *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 assujetti 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.[5]

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 τ 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

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

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[5] 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 vitesse 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. See chapter 9 of the present book.

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 Ω" in an isothermal transformation. The analogy between mechanics and thermodynamics led Duhem to choose the name "*thermodynamic potential* of the system" for the function Ω.[6]

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.*
>
> *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.*[7]

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 Ω became $F = E(U - TS)$, which was "Helmholtz's free energy" or Gibbs' ψ function. In the second case, $dW = pdv = d(pv)$, and the potential Ω became $\Phi = E(U - TS) + pv$, which was "nothing else but Gibbs' ζ function".[8]

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 Φ. The function F had to be considered as a function of volume v and temperature T, whereas the function Φ 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:

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[6] Duhem P. 1886, pp. 7-8.

[7] Duhem P. 1886, p. 9.

[8] Duhem P. 1886, pp. 9-10.

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

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 Φ with regard p and T:

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

Entropy and volume could be expressed as derivatives of the potential Φ, 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 α of dilatation under constant pressure", "the coefficient ε of compressibility", and "the coefficient α' of dilatation under constant volume" in terms of derivatives of the potential Φ. Even specific heat at constant pressure was expressed in terms of the derivatives of the potential Φ:

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

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 Φ 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.[10]

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[9] Duhem P. 1886, pp. 10-13. There are some misprints in Duhem's text.

[10] 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."

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.[11]

Since the "Introduction" he had expressed his intellectual dissatisfaction with the lack of generality and the "lack of rationale" in previous theories about magnetism. He found that "Poisson's conceptual path" suffered from at least three "difficulties": complications in "basic hypotheses", a specific weakness in "mathematical deductions", and some disagreement with "facts". He acknowledged that W. Thomson and Gustav Kirchhoff had subsequently tried to overcome those difficulties, but they had merely assumed, at the outset, Poisson's equations, without any attempt to derive the equations from "more general theories". According to Duhem, both theoretical and experimental flaws threatened the logical and physical foundations of the received magnetic theories. He would have founded his theory on the "unquestioned laws" ruling the interactions between magnets, and on the "unquestioned principles" ruling thermodynamics.[12]

The first chapter, "Potentiel thermodynamique d'un système qui renferme des aimantes", opened with a very general section dealing with "Quelques propositions de Thermodynamique", where the pivotal concept of "*non-compensated transformation*" *dN* was at stake once

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[11] 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.

[12] Duhem P. 1888, p. 1.

again. He introduced a function τ, which had the properties of energy or work, and was linked to the function N by the relation $dN = d\tau / T$, and rephrased the two laws of Thermodynamics in order to put τ into prominence. That term was named *"non-compensated work"*, or better *"the uncompensated work performed in the course of an isothermal transformation"*. In the case of external forces stemming from a potential *W*, he could rely on the potential or the function "of state" Ω he had introduced in 1886:

$$d\tau_e = -dW, \quad d\tau = -E\, d(U - TS) - dW,$$
$$d\tau = -d\left[E(U - TS) + W\right], \text{ and } d\tau = -d\Omega.$$[13]

The relationships among τ, *N*, and Ω, in the context of isothermal transformations, was summarized by Duhem in the following passages.

> … *le travail non compensé effectué durant une transformation isothermique est alors la variation changé de signe d'une fonction de l'état du système* Ω.
> Nous donnerons à cette fonction Ω le nome de *potentiel thermodynamique* du système.
> Moyennant ces conventions, la condition d'après laquelle *dN* doit toujours être positif peut s'énoncer ainsi :
> *Pour qu'un système dont tous les points sont à la même température absolue soit en équilibre stable, il suffit que le potentiel thermodynamique de ce système ait la plus petite valeur qu'il peut prendre à la température considérée.*[14]

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".

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[13] Duhem P. 1888, pp. 3-4.
[14] Duhem P. 1888, p. 4.

> 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*.[15]

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 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*.[16]

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 con-

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[15] Duhem P. 1888, p. 5.

[16] Duhem P. 1888, p. 12.

sistent with that principle, we do not know whether that transformation will really take place or not".[17]

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.[18]

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 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

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[17] Duhem P. 1888, pp. 12-13.

[18] Duhem P. 1888, p. 13.

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".[19]

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

$$
\begin{aligned}
&A = f_\alpha(\alpha,\beta,\ldots\ldots,\lambda,\vartheta)\\
&B = f_\beta(\alpha,\beta,\ldots\ldots,\lambda,\vartheta)\\
&\ldots\ldots\\
&L = f_\lambda(\alpha,\beta,\ldots\ldots,\lambda,\vartheta)\\
&\Theta = f_\vartheta(\alpha,\beta,\ldots\ldots,\lambda,\vartheta).
\end{aligned}
$$
[20]

From the thermodynamic point of view, every infinitesimal transformation involving the generalized *displacements* $\delta\alpha,\ \delta\beta,\ \ldots,\ \delta\lambda$ 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:

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

.

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[19] 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.

[20] Duhem P. 1891, p. 233-4.

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

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

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

wherein

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

The new alliance between Mechanics and Thermodynamics led to a sort of symmetry between thermal and mechanical quantities. The *n+1* functions R_α, R_β, …, R_λ, R_ϑ, which Duhem re-wrote as R_α, R_β, …, R_λ, *C*, played the role of *generalized thermal capacities*, and the last term *C* was nothing else but the ordinary thermal capacity: in some way, the second typographical choice re-established the traditional asymmetry.[21]

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, …, L, Θ, and the series R_α, R_β, …, R_λ. The mathematical equivalence expressed by the last equations required the existence of a function of state *U*, namely "a uniform function of α, β, …, λ, and ϑ, so that $E(dQ+dU)= d\tau_e$". Coming back to the physical point of view, the mathematical equivalence

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[21] Duhem P. 1891, p. 234.

corresponded to "the principle of equivalence between work and heat".[22]

Another set of equations proved to be useful in the building up of Duhem's Thermodynamics. The Lagrangian parameter ϑ 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 ϑ. This means that the function entropy, a "uniform, finite, and continuous function of α, β, ..., λ, and ϑ", had to be defined as

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

New mathematical equivalences could be derived:

$$\frac{\partial}{\partial\beta}\frac{R_\alpha}{F(\vartheta)} = \frac{\partial}{\partial\alpha}\frac{R_\beta}{F(\vartheta)}, \text{ or } \quad \frac{1}{F(\vartheta)}\left(\frac{\partial R_\alpha}{\partial\beta} - \frac{\partial R_\beta}{\partial\alpha}\right) = 0,$$
$$\frac{1}{F(\vartheta)}\left(\frac{\partial R_\alpha}{\partial\vartheta} - \frac{F'(\vartheta)}{F(\vartheta)} R_\alpha\right) = \frac{1}{F(\vartheta)}\frac{\partial C}{\partial\alpha}.^{23}$$

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

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[22] Duhem P. 1891, p. 235.

[23] Duhem P. 1891, pp. 235-6. Here a sort of asymmetry between *mechanical* and *thermal* parameters emerges.

> *et dans lequel une transformation élémentaire à partir d'un état d'équilibre dégage une quantité de chaleur*
>
> $$dQ = -\left[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \ldots\, R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta\right];$$
>
> *pour que ce système vérifie les deux principes fondamentaux de la Thermodynamique, il faut et il suffit que les deux quantités*
>
> $$\left(R_\alpha + \frac{A}{E}\right)\cdot\delta\alpha + \left(R_\beta + \frac{B}{E}\right)\cdot\delta\beta + \ldots \left(R_\lambda + \frac{L}{E}\right)\cdot\delta\lambda + \left(C + \frac{\Theta}{E}\right)\cdot\delta\vartheta,$$
>
> $$\frac{R_\alpha}{F(\vartheta)}\cdot\delta\alpha + \frac{R_\beta}{F(\vartheta)}\cdot\delta\beta + \ldots \frac{R_\lambda}{F(\vartheta)}\cdot\delta\lambda + \frac{R_\vartheta}{F(\vartheta)}\cdot\delta\vartheta$$
>
> *soient deux différentielles totales.*[24]

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

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

As Duhem remarked, this equation says that the *n+1* functions f_α, f_β, …, f_λ, and f_ϑ, which define the differential coefficients *A*, *B*, …, *L*, and Θ, "could not be chosen arbitrarily". In particular it suggests that "a uniform, finite, and continuous function $\mathrm{F}\,(\alpha,\beta,\ldots,\lambda,\vartheta)$ of *n+1* parameters α, β, …, λ, and ϑ there exist". The gradient of F can be written component by component, taking care of the specific behaviour of the component Θ, which was "independent of the function F":

$$A = \frac{\partial}{\partial\alpha}\mathrm{F}\,(\alpha,\beta,\ldots,\lambda,\vartheta),\ B = \frac{\partial}{\partial\beta}\mathrm{F}\,(\alpha,\beta,\ldots,\lambda,\vartheta),\ \ldots\ L = \frac{\partial}{\partial\lambda}\mathrm{F}\,(\alpha,\beta,\ldots,\lambda,\vartheta).$$[25]

What do we know about the functions Θ 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

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[24] 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.

[25] Duhem P. 1891, pp. 237-8. In terms of vector calculus, if ***K***=(*A*, *B*, …, *L*) and $\nabla \times K = 0$, then $K = \nabla\mathrm{F}$, just because $\nabla \times \nabla\mathrm{F} = 0$ for every F.

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":

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

$$\frac{\partial C}{\partial \beta}=\ldots,\ \ldots\ldots,\ \frac{\partial C}{\partial \lambda}=\ldots$$

The last set of equations shows how deeply entangled were the *thermal* and *mechanical* properties of a physical system.[26]

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 α, β, …, and λ in order to keep at rest the whole system when the parameter ϑ changed. In this case, "the mere change of ϑ 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, …, L) shows us the persistence of the deep connection between mechanical and thermal effects, even when the formal symmetry between them was weakened:

$$\frac{\partial C}{\partial \alpha}=-\frac{T}{E}\frac{\partial^2 A}{\partial T^2},\quad \frac{\partial C}{\partial \beta}=-\frac{T}{E}\frac{\partial^2 B}{\partial T^2},\ \ldots\ \ldots,\quad \frac{\partial C}{\partial \lambda}=-\frac{T}{E}\frac{\partial^2 L}{\partial T^2}.$$[27]

According to Duhem, "the mechanical determination of the system" required firstly the specification of the function F , and then the deduction of the generalized forces A, B, …, L, and Θ, and the "thermal coefficients" R_α, R_β, …, and R_λ. 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

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[26] Duhem P. 1891, pp. 238-9.

[27] Duhem P. 1891, pp. 239-41.

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 F and the function $\Theta = f_{\vartheta}(\alpha, \beta, \ldots, \lambda, \vartheta)$.

> 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_{ϑ}*, 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*.[28]

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 α, β, …, λ and ϑ, had led to the equations of equilibrium for the *n+1* functions *A*, *B*, …, *L*, and Θ, and the *n+1* functions R_α, R_β, …, R_λ, and R_ϑ. That procedure could be reversed: instead of starting from the *geometrical-thermal* parameters α, β, …, λ and ϑ, in order to arrive at the *dynamical* conditions of equilibrium for *A*, *B*, …, and *L*, he showed that he could start from the *dynamical-thermal* parameters *A*, *B*, …, *L*, and ϑ, in order to arrive at the *geometrical* equations of equilibrium on α, β, …, and λ.[29]

In Duhem's representation, physical events took place in a sort of abstract hyper-space at *n+1* components: *n mechanical* components α, β, …, and λ, and one *thermal* component ϑ. The Lagrangian representation of phenomena in space and time required *n* generalized parameters α, β, …, and λ, 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,

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[28] 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).

[29] Duhem P. 1891, pp. 259-61.

Duhem did not take into account time as an explicit parameter; this role was played by the *thermal* parameter ϑ.

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 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.[30]

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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[30] 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.

7. 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 principe 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.[1]

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.[2]

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

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[1] 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.

[2] 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."

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.[3]

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, …, and L the elements of the first set, and α, β, …, and λ the elements of the second. Matter could be described geometrically by some functions of Lagrangian parameters α, β, …, λ: among state quantities Duhem distinguished those which appeared explicitly in those equations from those which did not appear. He reserved the labels α, β, …, and λ for the former, and introduced new labels a, b, …, l for the latter: in some way he separated geometrical quantities from other quantities. 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

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[3] 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)

locate the different levels of heat. Moreover, temperature could not be univocally defined: after having defined a temperature ϑ, any continuous and increasing function $\Theta = f(\vartheta)$ could play the role of temperature.[4]

In the third chapter he started from a complex system Σ, which was isolated in space, and could be looked upon as the composition of two "independent systems" *S* and *S′*. If the kinetic energy of Σ was simply the sum of the kinetic energies T and 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*:

$$\begin{aligned} \Upsilon = {} & U(\alpha,\beta,\ldots,\lambda;a,b,\ldots,l) + U'(\alpha',\beta',\ldots,\lambda';a',b',\ldots,l') \\ & + \Psi(\alpha,\beta,\ldots,\lambda;a,b,\ldots,l;\alpha',\beta',\ldots,\lambda';a',b',\ldots,l') \end{aligned}$$

The total energy of Σ was $\varepsilon = \Upsilon + (1/E)(\mathsf{T} + \mathsf{T}')$, and generalised forces could be derived from the potential of interaction Ψ:

$$\begin{aligned} & E\frac{\partial\Psi}{\partial\alpha} = -A, \quad E\frac{\partial\Psi}{\partial\beta} = -B, \ldots \quad \ldots, E\frac{\partial\Psi}{\partial\lambda} = -L, \\ & E\frac{\partial\Psi}{\partial a} = -\mathsf{A}, E\frac{\partial\Psi}{\partial b} = -\mathsf{B}, \ldots \quad \ldots, E\frac{\partial\Psi}{\partial l} = -\mathsf{L} \end{aligned}$$

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

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[4] 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 ϑ has the same value everywhere". In the second chapter, he tried to clarify some basic physical concepts: closed cycle, work, kinetic and potential energies, internal energy, the additive property of work, and the principle of the conservation of energy. He stressed the status of "physical hypothesis" of that principle: it was submitted to experience, and it could not be demonstrated, but only put forward by means of some physical considerations. (*Ibidem*, pp. 291-307)

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

Duhem represented the work done by forces and influences as

$$\left(A\cdot u+B\cdot v+\ldots+L\cdot w\right)dt \quad \text{and} \quad \left(\mathsf{A}\cdot\varphi+\mathsf{B}\cdot\chi+\ldots+\mathsf{L}\cdot\psi\right)dt.$$[5]

In the more complex case of three "partial systems S_1, S_2, S_3", the potential Ψ 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 Σ composed of "*n* independent systems S_1, S_2, …, S_n". Conversely, those definitions and remarks allowed Duhem to outline, at least in part, the features of a "complex system".

> *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.*[6]

The key entity was the total energy

$$\varepsilon=\Upsilon+\frac{1}{E}\left(\mathsf{T}+\mathsf{T}'\right)=U+U'+\Psi+\frac{1}{E}\left(\mathsf{T}+\mathsf{T}'\right).$$

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

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[5] 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 Ψ 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* Σ *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."

[6] Duhem 1892, p. 315.

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.[7]

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

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

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

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

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_ϑ 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

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

The last two sets of equations specified the terms which appeared in the fundamental equation $E\big(dQ + \delta U\big) = d\tau$, which was nothing else but

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[7] 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."

the first principle of Thermodynamics or “the law of equivalence between heat and work”.[8]

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

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

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

Since the first set of equations corresponded to Lagrange’s equations of rational mechanics, the derivation seemed successfully achieved. Nevertheless, a question arose: could the physical derivation be reversed? In other words, are we sure that, when ordinary mechanics is at stake, all thermal coefficients vanish? At that stage, Duhem could not satisfactorily answer the question, and he acknowledged that further theoretical investigations were required. 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.[9]

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-

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[8] Duhem 1892a, pp. 320-1.

[9] 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.”

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.[10] Poincaré 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.[11]

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

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[10] 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 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.

[11] Poincaré H. 1892, pp. V, XII-XIV, and XVIII.

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 Clauisus' theorem cannot be explained by Lagrange equations".[12]

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.[13]

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

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[12] See Poincaré H. 1892, pp. 98, 100, 103, 211-2, 392, and 422. He made extensive use of "Massieu characteristic functions".

[13] 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 Brahman, who tried to understand "our old Europe" looking through the windows of steamers or fast trains "during a swift tour".

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.[14]

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 (α, β, ..., λ, and ϑ) to a new state (α', β', ..., λ', and ϑ'), 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 $R_\alpha = R_\beta = ... = R_\lambda = 0$, automatically $dQ = 0$, and equations of "classical rational Mechanics" followed, where no reference to heat or temperature was made.[15] 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

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[14] 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.

[15] Duhem 1893a, pp. 337, 345, 355, and 357-8.

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".[16]

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 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.[17]

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

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[16] Poincaré H. 1893, p. 534.

[17] Poincaré H. 1893, pp. 534-5.

deduction wherein "we find reversibility at the outset, and irreversibility at the end".[18]

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 $\alpha,\ \beta,\ \ldots,\ \lambda$ and ϑ, which seemed a step backward with regard to the more general choice of parameters $\alpha,\ \beta,\ \ldots,\ \lambda,\ a,\ b,\ \ldots,\ l$ 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

$$\begin{array}{lll} \Upsilon_1(\alpha_1,\beta_1,\ldots,\lambda_1,\vartheta_1), & \Sigma_1(\alpha_1,\beta_1,\ldots,\lambda_1,\vartheta_1), & \mathsf{F}_1(\alpha_1,\beta_1,\ldots,\lambda_1,\vartheta_1) \\ \Upsilon_2(\alpha_2,\beta_2,\ldots,\lambda_2,\vartheta_2), & \Sigma_1(\alpha_2,\beta_2,\ldots,\lambda_2,\vartheta_2), & \mathsf{F}_1(\alpha_2,\beta_2,\ldots,\lambda_2,\vartheta_2) \end{array}.$$

As in Duhem's 1892 approach, the internal energy $U = \Upsilon_1 + \Upsilon_2 + X_{1/2}$ 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 $\mathsf{U} = U + U' + \Psi$ had another kind of interaction term Ψ, apart from the internal energy U' of the environment.[19]

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

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[18] 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.

[19] Duhem 1894a, pp. 208-11. The new term $X_{1/2}$ corresponded to the old term Ψ 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.

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, …, l …* variaient seules, les variables α, β, …, λ gardant des valeurs fixes. De la sorte, le mot *mouvement* s'oppose non pas au mot *repos*, mais au mot *équilibre*.[20]

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 $f_\alpha, f_\beta, ..., f_\lambda$:

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

The new functions represented "passive resistances to be overcome by the system". Those resistances depended on basic parameters α, β, …, λ, ϑ, their time derivatives $\alpha', \beta', ..., \lambda'$, 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 $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + ... + f_\lambda \cdot d\lambda$ 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.[21]

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[20] Duhem 1894a, p. 222.

[21] Duhem 1894a, pp. 223-4. In this case the symbolic mismatch seems even more puzzling: in 1891 Duhem had made use of the functions $f_\alpha, f_\beta, ..., f_\lambda$ in order to express explicitly the dependence of external forces on the basic parameters, namely

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

> Lorsque l'état des corps extérieurs est donné à chaque instant t, les résistances passives deviennent des fonctions des variables
> $\alpha, \beta, \ldots, \lambda, \vartheta, \alpha', \beta', \ldots, \lambda', t$.
> Les équations (2) deviennent lors des équations différentielles du second ordre, qui détermineraient les valeurs des variables $\alpha, \beta, \ldots, \lambda, \vartheta$, 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.[22]

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:

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

In the ϑ-component of this series of equations, the term representing the passive resistance was missing: it had not been put forward at the beginning, and it could not be found at the end.[23]

$A = f_{\alpha}(\alpha, \beta, \ldots, \lambda, \vartheta)$ and so on. In 1894, the new *dissipative forces* $f_{\alpha}, f_{\beta}, \ldots, f_{\lambda}$ had to be added to the already existing forces *A'*, *B'*, …, *L'*.

[22] Duhem 1894a, pp. 224-5.

[23] Duhem 1894a, pp. 225-6.

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

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

in 1894

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

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

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

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

Duhem could finally identify the work $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \ldots + f_\lambda \cdot d\lambda$ with Clausius' "uncompensated work".

> Clausius a donné à la quantité $-\left(f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \ldots + f_\lambda \cdot d\lambda\right)$, 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 $E\,F(\vartheta)dS$ est au contraire, pour lui, le travail compensé accompli durant cette même modification.[24]

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[24] Duhem 1894a, pp. 228-9.

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

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

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".[25]

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

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

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[25] Duhem 1894a, p. 229.

ciple stem from the laws of Dynamics in a satisfactory way". According to Duhem, the latter had attained more success.[26]

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.[27]

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 reinterpretation 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.[28]

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[26] Duhem 1894a, pp. 284-5.

[27] Duhem 1894a, p. 285.

[28] Duhem 1894a, p. 285.

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".

8. FURTHER STRUCTURAL ANALOGIES

In the meantime, early in the 1890s, Duhem had undertaken another theoretical pathway: it appeared as a different pathway, but it was, in reality, a different branch in the same design of unification. We are dealing here with chemistry, in particular the links between chemistry and physics. The long paper Duhem published in the *Revue de questions scientifiques* under the title "Notation atomique et hypothèses atomistiques" in 1892 was a sort of historical and critical reconstruction of chemistry in the nineteenth century. From the outset he pointed out an intrinsic difference between physics and chemistry: if the former tried to "represent the laws ruling certain phenomena", the latter tried "to class the substances". In some way, that difference was not so distant from the difference "between physiology and morphology". Nevertheless, both physics and chemistry were parts of his wide-scope design: he would have pursued the unification of the two sciences under "the principles … of mathematical physics".[1]

The last section, "On atomistic hypotheses" was the conceptual core of the paper, and the adjectives "atomic" and "atomistic" were at stake. Duhem started from a linguistic specification: the expressions "*atomic weight*" and "*atomicity*" could easily be replaced by "*equivalent weight*" and "*valence*". In other words, he tried to remove the concept

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[1] Duhem P. 1892c, p. 392. With regard to the relationship between Duhem and the Belgian scientific journal *Revue des questions scientifiques*, see Stoffel J-F. 2002, p. 330: "Duhem trouva donc auprès de la Societé scientifique de Bruxelles un espace de liberté et l'on peut dire que que la *Revue des questions scientifiques* constitua pour lui, Durant les années 1890, son principal lieu de publication pour ses travaux philosophiques at pour ses écrits les plus engagés". The Society was founded in 1875, and the *Revue* in 1877 (see *Ibidem*, p. 331).

of atom from chemistry and physics, even though he acknowledged that the recent developments in chemistry had stemmed from "hypotheses on the atomic constitution of matter". According to Duhem, hypotheses on the discontinuous or continuous structure of matter were philosophical rather than scientific issues. Then he pointed out some difficulties which emerged from an atomistic interpretation of valence: how could some facts be explained? Carbon, for instance, "has valence four in methane and carbonic acid but is bivalent in carbon monoxide" Moreover, in some compounds there was more than one occurrence of a given element, and the element appeared with different valences. This was not consistent with the hypothesis of valence as "the specific number of atomicity" of a given atom.[2]

Duhem interpreted valence as a relational property: there was "no valence outside a combination", and valence came into play only when a substance entered into a combination. Furthermore, another question was at stake: how could the atomic hypothesis explain the fact that different atomic structures gave rise to very similar macroscopic structures? In this case, the microscopic level could not be looked upon as the explanation of the macroscopic one. According to Duhem, all these difficulties could be overcome by interpreting "atomic notation" as a sort of orthography, based on the two "notions of *chemical analogy and substitution*". Those concepts were useful "for classifying chemical compounds": without any assumption about the actual "nature of bodies", chemistry could become independent of "any philosophical school".[3]

The last passages of the paper had a sharp meta-theoretical nature, and consisted of a collage of quotations from the chemist Sainte-Claire Deville. Duhem insisted that scientists had to confine themselves to "establishing analogies, taking note of similarities and differences", in order to establish a classification which is always "incomplete" in its nature. At the same time, the experiments had to check the soundness of the principles, and cast light on their possible "defaults and inaccuracies". In no way could scientists believe in their hypotheses, which were only provisional tools: over time, all of them "would have dis-

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[2] Duhem P. 1892c, pp. 439-40, 447, and 449,

[3] Duhem P. 1892c, pp. 450-2, Duhem remarked that sodium nitrate and calcium carbonate were molecules endowed with different constitutive formulas, but at the macroscopic level, they showed "the same crystal lattice".

appeared" from the stage of science. In no way had scientists to reify "abstractions which are imposed by the weakness of our mind". Obviously, the concept of atom was one of these abstractions, and abstractions became "dangerous when we forget their origin" and history. In some way, the history of science was looked upon as the judge of science itself: historical awareness could prevent scientists from pursuing a misleading "scientific mysticism". [4]

Even in the first part of the book Duhem published in 1893, *Introduction à la mécanique chimique*, he put forward a historical rather than "logical" approach to chemistry: this meta-theoretical attitude was one of the hallmarks of his scientific practice. He found that "the content of a physical law" could be better appreciated keeping the reader in contact with the "efforts" required in order to attain it, and the "mistakes" avoided or overcome. The main steps in the history of "chemical mechanics" dealt with the dichotomy exothermic-endothermic. In the first stage, corresponding to the first half of the nineteenth century, exothermic transformations were identified with chemical combinations, and endothermic transformations with chemical decompositions. In the second stage, around the middle of the century, the theoretical link between the couples exothermic-endothermic and combination-decomposition was broken: exothermic transformations were identified with spontaneously occurring chemical reactions, and the endothermic with "indirect" reactions. In the third stage, corresponding to the time at which Duhem was writing, the role of temperature was given prominence: when the temperature rises, an "exothermic compound should undergo an increasing dissociation", and an "endothermic compound should be more easily formed". Three issues were at stake: the attempt to unify phys-

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[4] In the end, Duhem reported Sainte-Claire Deville's passages from his 1867 "Leçons sur l'affinité". One of them is particularly meaningful, beacause Duhem endorsed it without reservation. See Duhem P. 1892c, pp. 453-4: "L'hypothèse des atomes, l'abstraction de l'affinité, des forces de toute sorte que nous faisons présider à toutes les reactions des corps que nous étudions, sont des pures inventions de notre esprit, des noms que nous faisons substance, des mots auxquels nous prêtons une réalité. Toutes ces hypothèse, toutes ces abstractions ne sont heureusement pas indispensables." It is worth mentioning that, in 1880, in a brief *Note* sent to *Comptes Rendus de l'Académie des Sciences*, Sainte-Claire Deville claimed that he could accept "neither atoms, nor molecules, nor forces": he could not rely on entities he could "neither see nor imagine". (Sainte-Claire Deville H. 1880, p. 342)

ics and chemistry, the role of Thermodynamics in that unification, and the already outlined design of a generalized physics for every kind of material transformation. These issues were mutually intertwined: could a general theory of transformations not entail some sort of unification between physics and chemistry?[5]

Another sensitive issue was represented by the relationship between the chemical concept of "affinity" and the physical concept of "cohesion". Claude Louis Berthollet was credited by Duhem with having been the first to put forward a "chemical Mechanics": it was based on the general "principles" of Newton's "celestial Mechanics", and had recently been translated into Laplace and Poisson's recent "physical Mechanics". Duhem appreciated Berthollet's unified explanation for physical "changes of state" and "chemical phenomena in the strict sense". Although he did not trust in the specific mechanical models put forward by Laplace and Poisson, in general terms he shared Berthollet's meta-theoretical expectation that "the more the principles stemming from the chemical theory are general, the more they will look like those of mechanics". Berthollet had modified the ancient view, calling into play the superposition of physical cohesion and chemical affinity. In other words, *chemical* processes of combination or decomposition could be accompanied by physical processes of contraction or dilatation: both of them involved transfers of heat.[6]

Duhem credited Lavoisier and Laplace with having been the first to leave aside "scholars' philosophical ideas on the nature of caloric", because "physical consequences" did not depend on them. In the first decades of the nineteenth century, heat had been assumed to undergo some kind of conservation over time, but in the 1850s Clausius had shown that "internal energy" had the property "attributed to heat by the ancient physicists": it depended only on the initial and final state of the transformation. The amount of heat entering a body could trigger off three different processes: an increase of "free heat" or tempera-

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[5] Duhem P. 1893b, pp. v-vii.

[6] Duhem P. 1893b, pp. 2, 8, 9, 11, and 19-24. Duhem traced back the conceptual root of Berthollet's theory to Newton's famous XXXI *Query* to be found at the end of his *Opticks*. There the grand savant had envisaged a short-range force, or a "*molecular attraction*", beside long-range universal gravitation. Duhem cautiously specified that "the nature of molecular action" was "almost unknown" at present (*Ibidem*, p. 10). He quoted from Berthollet's1803 *Essai de statique chimique*, p. 2.

ture, macroscopic or external work, and microscopic work done by "molecular forces". In terms of more ancient concepts, the last two terms corresponded to the increase of "latent caloric". In Duhem's historical reconstruction, Clausius' theory represented a re-interpretation of the ancient "antagonism between molecular attraction and heat", and a further step towards unification.[7]

Marcelin Berthelot had recently upheld the different nature of chemical and physical processes, but Duhem insisted that thermodynamics required a sort of symmetry between chemistry and physics. He followed Sainte-Claire Deville, who had emphasised the strong analogy between "the mechanism of chemical reactions and the mechanism of physical changes of state". Duhem also devoted two short chapters to the "kinetic theory of gases put forward by August Krönig and Clausius, and perfected by Boltzmann and Maxwell". The "kinetic" theory and the theory of "molecular attraction" stemmed from the same attitude towards physics, which involved hypotheses on the hidden structure of matter. An invisible world, described by specific microscopic mechanical models, had to explain the macroscopic effects "appreciated by our senses". He would have turned upside down the "method" or the "ideal" of mechanical models, which was based on two pillars, the first being theoretical, and the second meta-theoretical: a set of "few, simple mechanical hypotheses", and the belief that they are "real *explanations*". Duhem's scientific method did not aim at "*explaining* phenomena but *classifying* them".[8] Duhem's struggle against mechanical models was very passionate.

> Pourquoi chercher à remplacer par des constructions mécaniques les corps et leurs modifications, au lieu de les prendre tel que les sens nous les donnent, ou plutôt tels que notre faculté d'abstraire, travaillant sur les

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[7] Duhem P. 1893b, pp. 12-7, 26, and 29. The previous theory had assumed that atmospheres of caloric surrounded molecules of ordinary matter, and caloric attracted matter: atmospheres repelled each other, while matter attracted matter. From the thermal point of view, chemical combinations were looked upon as the defeat of thermal repulsion by material attraction, followed by "the emission of part of latent caloric". The prominence of thermal repulsion on material attraction led to decompositions: "the amount of latent caloric would grow at the expense of the body's free caloric or caloric coming from surrounding bodies". If combinations sent out caloric, decompositions absorbed caloric, according to a theoretical representation of caloric as some kind of substance endowed with a specific power. (See *Ibidem*, pp. 28-9)

[8] Duhem P. 1893b, pp. 52, 56, 58, 68, 74-5, 81, 87, and 89.

> données des sens, nous les fait concevoir ? Pourquoi se représenter la température comme la quantité d'un certain fluide libre ou comme la force vive d'un certain mouvement, au lieu de la regarder simplement comme cette propriété qu'a un corps de nous paraître plus ou moins chaud, de faire monter plus ou moins haut le mercure du thermomètre ? Pourquoi chercher à se figurer les changements d'état comme des déplacements, des juxtapositions de molécules, des variations de trajectoires, au lieu de se caractériser un changement d'état par le trouble qu'il apporte dans les propriétés sensibles et mesurables du corps : augmentation ou diminution de densité, absorption ou dégagement de chaleur, etc… ? Pourquoi vouloir que les axiomes sur lesquels toute théorie doit reposer soient des propositions fournies par la statique ou la dynamique, au lieu de prendre pour principes des lois fondées sur l'expérience et formulées par l'induction, quelle que soit d'ailleurs la forme de ces lois, quelle que soit la nature des concepts auxquelles elles font appel ?[9]

The ninth chapter of the book represents in some way the turning point of the book: the second Principle of Thermodynamics takes the centre of the stage, accompanied by the "critical" concept of "reversible transformation" or "series of states of equilibrium". Although that kind of transformations were "actually unworkable" and "very abstract", Duhem acknowledged that it was "impossible to make use of thermodynamics without making constant use of it". For a series of transformations leading from a state (a) to a state (b), he expressed the second Principle as

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}+\ldots+\frac{Q_n}{T_n}=S_a-S_b+P,$$

where the always positive quantity P corresponded to Clausius' "uncompensated work".[10] An isolated physical system was in equilibrium "if all possible transformations" could not "increase its entropy": Duhem stressed that the Principle was universal, and every design of "chemical mechanics" had to take it into account. In the case of isothermal transformations, the last equation could be written as

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[9] Duhem P. 1893b, p. 88.

[10] Duhem P. 1893b, pp. 93, 96 and 100.

$$\frac{Q_1+Q_2+\ldots+Q_n}{T_1}=S_a-S_b+P \quad \text{or} \quad \frac{Q}{T}=S_a-S_b+P \quad \text{or} \quad Q=T\left(S_a-S_b\right)+TP.$$

On the right-hand side, the first term could be interpreted as "*the amount of compensated heat*", and the second term as "*the amount of uncompensated heat*". From the mechanical point of view, the corresponding quantities $\vartheta=ET\left(S_a-S_b\right)$ and $\tau=ETP$ could be interpreted as "*compensated work*" and "*uncompensated work*". Duhem found that the second Principle could restore the symmetry between physics and chemistry: if mechanical equilibrium required that "*all virtual modifications*" performed a vanishing or negative work, thermodynamic equilibrium required that "*all virtual isothermal modifications*" performed a vanishing or negative uncompensated work.[11]

The *structural* analogy between Mechanics and Thermodynamics allowed Duhem to set up a structural analogy between Mechanics and Chemistry based on thermodynamic potentials. When no external work was involved, $\tau=F_a-F_b$, and Duhem found natural to label "*internal uncompensated work*" that difference. When the external forces could be derived from a potential Ω, the uncompensated work could be written as $\tau=\Phi_a-\Phi_b$, namely the difference between the values of a "total thermodynamic potential" $\Phi=F+\Omega$.

> *Un système est en équilibre stable si la valeur du potentiel thermodynamique total de ce système est un minimum parmi toutes les valeurs que la même quantité peut prendre à la même température.*
>
> Cette proposition est analogue à celle que l'on démontre en mécanique et qui s'applique aux systèmes soumis à des forces admettant un potentiel : *Un tel système est en équilibre stable lorsque le potentiel des forces auxquelles il est soumis a une valeur minima.*
>
> L'analogie entre la statique chimique et la statique mécanique est complète.[12]

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[11] Duhem P. 1893b, pp. 104 and 106-8.

[12] Duhem P. 1893, pp. 112-3. As already stressed, that *structural* analogy could in no way be confused with attempts to transfer specific *mechanical models* from mechanics to thermodynamics and chemistry. Duhem attempted to generalise "Gibbs, Maxwell and von Helmholtz's methods", and Maxwell and Helmholtz's concepts of "available energy" and "*freie Energie*". The old "thermo-chemistry" could give way to a "chemical mechanics based on thermodynamics" (*Ibidem*, pp. 114-6).

In the last chapters of the book, Duhem widened the scope of his theoretical, meta-theoretical and historical inquiry: the complex interplay among Analytical Mechanics, Thermodynamics and Chemistry was extended to electricity, in order to clarify the difference between the so-called *"voltaic heat"* and *"chemical heat"*. The second Principle offered the solution even in this case, because chemical heat was the algebraic sum of "compensated heat and uncompensated heat". What was called "voltaic heat" was nothing else but *"chemical uncompensated heat"*. According to Duhem, what differentiated the "theory of the thermodynamic potential" from the old "thermo-chemistry" could be summarized as follows: the former "replaces the uncompensated heat to total heat". He found that, when we are dealing with *"very energetic reactions*, the amount of uncompensated heat is close to the amount of total heat", and they have the same mathematical sign. Moreover, very energetic reactions "occur by themselves", and send out heat: in other words, they are exothermic. The old thermo-chemistry represented only "a limiting case" of the new theory, when chemical reactions are particularly "violent".[13]

The last chapter also raised a different query, which had emerged from experiments performed at high temperatures: the phenomenon of "false equilibrium". What was Duhem's concept of "false" equilibrium? Thermodynamics forbade some transformations, and nobody had ever observed such kind of forbidden transformations. On the contrary, when some transformations were permitted by the theory, sometimes they did not happen. In some way, the system kept itself in equilibrium even when it should not: that equilibrium corresponded to Duhem's "false" equilibrium. In other words, when "the system should be in equilibrium, it actually stays in equilibrium", but it could stay in equilibrium "even when, according to the theory, it

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[13] Duhem P. 1893b, pp. 118-20, 123, 131, 137 and 139. It is worth mentioning that the identification of electric currents with dissipative effects was consistent with the electromagnetic interpretations put forward by some scientists in the last decade. In the wake of Maxwell, the British physicists Poynting and Heaviside looked upon electric currents in conductors as the side-effect of a mechanical breakdown, namely a loss of elasticity, in the passage from dielectric media to conducting media. Heaviside's specific model of aether as an elastic medium stemmed from a theoretical approach quite far from Duhem's *structural* analogies based on Analytical Mechanics. Nevertheless, from the point of view of energy and its properties, their interpretations were mutually consistent. See Poynting J.H. 1885, pp. 278 and 284, and Heaviside O. 1893, p. 17.

should not". Duhem qualified the former as "true equilibrium", and the latter as "false equilibrium". The concept of "false" equilibrium allowed Duhem to interpret chemical reactions which were "accompanied by a powerful release of heat". We are dealing here with explosions. Cases of this kind were in no way unusual: when mixtures of hydrogen and oxygen, or hydrogen and chlorine, reached their "true" equilibrium, namely water and muriatic acid, they released such a great amount of heat as to trigger off an explosion. In Duhem's theoretical framework, an explosion was therefore a passage "from a state of false equilibrium to a state of true equilibrium", wherein "a remarkable amount of heat" was released. The theory was "fruitful" because it could account for sudden and disruptive events left unexplained by the old theories.[14]

At the end of this detailed inquiry into the history of Mechanics, Thermodynamics and Chemistry, Duhem drew two conclusions, wherein historical and meta-theoretical remarks were mutually interconnected. On the one hand, he remarked that scientific theories, although definitely provisional, are notwithstanding fruitful. On the other hand, scientific practice could not have survived without theoretical frameworks, no matter how provisional, incomplete and even flawed they were. This fact explained why scientists had sometime tried to save a flawed theory at any cost when a better theory was not yet at hand.

> L'histoire du développement de la physique nous montre qu'une théorie serait bien présomptueuse en se flattant d'être définitive ; nous ne voyons guère les théorie s'élever que pour crouler. Mais, en s'écroulant, une théorie qui a été construite avec le désir sincère de parvenir au vrai, ne disparaît jamais complètement ; parmi ses débris se trouvent toujours des matériaux propres à entrer dans la composition de quelque autre système plus parfait et plus durable. […]

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[14] Duhem P. 1893b, pp. 157-9 and 173-4. In previous pages Duhem had described some processes giving rise to "false" equilibrium. See *Ibidem*, p. 155: "La décomposition de l'eau absorbe de la chaleur ; lors donc que l'on élève la température d'un mélange d'oxygène et d'hydrogène, et si nous faisons croitre graduellement sa température, nous n'y déterminerons tout d'abord aucune réaction chimique ; puis, tout à coup, lorsque la température atteindra environ +500°C, une partie du mélange gazeux passera avec explosion à l'état de vapeur d'eau."

> Il est rare que les contradictions de l'expérience suffisent à débarrasser la science d'une théorie erronée ; les partisans de cette théorie trouvent toujours quelque faux-fuyant pour tourner, en feignant de les interpréter, les faits qui les convainquent d'erreur; […] ; mais il faut les attribuer surtout au besoin qu'a l'esprit humain de grouper tant bien que mal les phénomènes qu'il observe autour de quelques idées ; lorsqu'il a ainsi construit un système, il le conserve, en dépit des démentis que les faits lui infligent, tant qu'une théorie plus complète, groupant dans un ordre plus satisfaisant de plus nombreuses données expérimentales, ne lui a été proposée.[15]

Meta-theoretical issues were really at stake in the contemporary debate on physical chemistry: they were triggered off by specific theoretical issues like the reliability of specific mechanical models, and the role of entropy. In the 1890s, Berthelot faced explicitly the second issue, and Wilhelm Ostwald the first one: Planck faced both of them.

In 1894, Berthelot sent a paper to the *Comptes Rendus de l'Académie des Sciences*, which dealt with the thermodynamic interpretation of chemical reactions. From the outset, he tried to face some "contradictions" involving the widespread point of view that "chemical actions are frequently accompanied by release of heat". In order to explain the presence of "combinations realised by release of heat", and "combinations realised by absorption of heat", Berthelot put forward his fundamental hypothesis: different kinds of heat had to be taken into account. In brief, he established the distinction between "heat of purely chemical nature" and "heat of different nature" ("quantités de chaleur étrangères").[16]

Among the different sources of "external heat", he listed "external mechanical work", and "purely physical changes of state". These kinds of heat had to be subtracted from "the rough heat", in order to compute "the chemical heat in its strict sense". It was by means of the purely chemical heat that chemical phenomena could be classed, whenever the system was "on the threshold of dissociation". He therefore defended his "experimental principle of maximum work", wherein the word "work" had the same meaning as "energy" or "heat". For the moment he confined himself to solid bodies, as heat released in the combination was "noticeably independent from temperature".

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[15] Duhem 1893b, p. 176.

[16] Berthelot M. 1894, pp. 1378-9.

> Si donc nous envisageons plusieurs systèmes différents de combinaisons solides, engendrées par la combinaison des mêmes éléments, soient Q, Q′, Q′′, … les quantités de chaleur dégagées par la formation de chacun de ces systèmes respectifs, le principe de travail maximum signifie que le système définitif vers lequel tendra la combinaison des éléments sera celui pour lequel Q est le plus grand possible : Q > Q′ > Q′′ ….[17]

According to Berthelot, in a transformation from a state (a) to a state (b), the heat released K was submitted to the inequality $K > T(S_a - S_b)$, and the quantity $K - T(S_a - S_b)$ corresponded to "the energy transformable into work". The introduction of entropy led only to "a new utterance" for the old "principle": in brief, what he had labelled "*chemical heat*" was "noticeably equivalent to heat transformable into work". Nevertheless, the mathematical equivalence did not correspond to a conceptual equivalence: he found that the law expressed in terms of entropy had a "more limited" scope, and its predictions were "more obscure". Some chemical systems did not have "computable entropy": entropy was a physical quantity suitable for "people involved … in mathematical physics". The intrinsic "discontinuity" of chemical processes did not allow scientists to trust in "a mathematical approach". Even in subsequent passages Berthelot insisted on the gap between mathematical algorithms and experimental practice: entropy was "an obscure concept", a quantity "disconnected from experience in most cases", and unsuitable for "the interpretation of most chemical phenomena".[18]

In the last passages of the paper, Berthelot acknowledged that entropy played "an essential role", and led to "predictions which elude the original principle of maximum work". Nevertheless, he found that the old principle should not be abandoned, and the "existence and importance" of "previous laws" should not be "neglected". In some way, he left the field of specific theoretical explanations, and entered the field of meta-theoretical or epistemological remarks. He claimed that "the discoveries of experimental sciences form a continuous chain", and "the positive facts and relations achieved in Thermochemistry today could not be overthrown". He went on with the same

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[17] Berthelot M. 1894, p. 1381.

[18] Berthelot M. 1894, pp. 1382-3 and 1385.

kind of reasoning, and stressed the possibility of improving old theories by means of “new facts and concepts”.[19]

Why and how the acknowledgement of the role of entropy could have impaired the continuity of the scientific practice, he did not say. Why and how entropy would have hampered the progress of Thermo-chemistry, he also did not say. Probably Berthelot chose the meta-theoretical level because he was aware that something important was at stake on that level: unlike Duhem, he did not trust in the alliance between mathematical physics and thermo-chemistry.

Historical reconstructions, meta-theoretical remarks, and a marked interest in the foundation of Thermochemistry were the distinctive features of an essay which Planck had published the year before. Planck looked upon Thermo-chemistry as a well defined field of research, which was one of the three branches of a recently established discipline, namely physical chemistry: the other two branches were Photo-chemistry and Electro-chemistry. In the essay, which was explicitly devoted to the foundations of Thermochemistry, *Grundriss der Allgemeinen Thermochemie*, he attempted “to develop concepts and propositions of Thermochemistry in close connection with the underlying facts”. He immediately specified that his theoretical inquiry was independent of specific atomistic conceptions”. According to Planck, “history had repeatedly shown that even the best hypothesis, once it has done its job, proves to be the most dangerous enemy of progress”, which necessarily “steps over” the hypothesis itself. Indeed he devoted thirty pages to a historical landscape which went from Lavoisier and Laplace to Wilhelm Ostwald and the Danish chemist Julius Thomsen.[20]

Planck relied on “the general validity of the two principles of thermodynamics” for all processes “which take place in Nature”. He specified that Berthelot’s “principle of maximum work” was only “similar” to the second principle of thermodynamics: they shared the same aim but were different with regard to their essential features. Both of them had been used by chemists in order to establish “the direction of natural transformations”. Nevertheless Berthelot had focus-

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[19] Berthelot M. 1894, p. 1392.

[20] Planck M. 1893, pp. III-IV and p. 1. Duhem is mentioned only at p. 117 in connection with the thermodynamic potentials he had discussed in his 1886 book.

sed only on "chemical energy", and distinguished it from "extraneous energies". The second principle did not need such a sharp split, and included all kinds of energy. Moreover, Berthelot's principle could not confine itself to the initial and final states of a transformation, but had to consider also intermediate states. As was well known, work was not a state function, and Berthelot's corresponding principle had to be applied to "every consecutive and infinitely small transformation" which occurred in the course of a finite transformation. In spite of Planck's confidence in the universal validity of the second Principle, he was dissatisfied with any cosmological extrapolation of the second Principle. For him, statements like "the energy of the universe is constant" and "the entropy of the universe increases" made "no sense from the physical point of view". He insisted on the irreversibility of definite natural processes, in particular chemical processes.[21]

In an appendix to the essay, which had already been published as a separate paper in a journal for physical and chemical education, Planck further specified his attitude towards the meaning of the second Principle. He stressed that the core of the principle did not lie in the "impossibility of transferring directly heat from a lower to a higher temperature". It could rather be found in the impossibility of reversing a natural process ("… sie überhaupt auf keinerlei Weise … zurückgeschafft werden kann"), even at the expense of mechanical work, without a contemporary transformation in the environment. According to Planck, any attempt to demonstrate this proposition was "totally and deceptively worthless". As meaningful instances of processes which were not completely reversible ("die nicht vollständig rückgängig zu machen sind") he mentioned "the freezing of undercooled water, the condensation of over-saturated steam, every explosive process", and in general "every transition to a stable condition of equilibrium". Chemistry was the natural seat of non-reversible processes ("der nicht vollständig rückgängig gemacht werden kann"): after a chemical reaction, chemical compounds could be led to a "previous initial condition", but "other permanent changes" took place in substances and instruments concurring to the reaction.[22]

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[21] Planck M. 1893, pp. 103, 105-6, and 113.

[22] Planck M. 1893, pp. 145-6. For Planck's detailed reference to his previous paper, see p. IV. For a detailed analysis of the meaning of Planck's adjectives "umkehrbar" and

In a paper sent to *Revue générale des Sciences pures et appliquées* in 1895, Ostwald, then professor of Physical Chemistry at Leipzig University, sharply criticised scientists who believed in "the Mechanics of atoms" as a suitable "key" for the comprehension of the physical world. To that mechanical world view, which Ostwald qualified as "physical materialism", he opposed "a new theory", which he labelled "energetics". Although he claimed that he would confine himself to "positive science", namely "exact sciences", in a subsequent passage he did not manage to refrain from stating that the rejection of a mechanical world view was an attack on "the materialistic view". The paper appears as an act of faith in his science of energy: rather than relying on atoms submitted to "laws of motions demonstrated for cosmic bodies", Ostwald relied on the discovery of "invariants", namely physical entities which preserved their values in the course of a physical transformation. He found that the claim to explain "all known physical phenomena by means of Mechanics" was "a vain enterprise".[23]

In the second half of the paper, Ostwald raised some crucial questions. As stressed by Poincaré in his 1893 paper, the most serious hindrance Mechanics had to face was represented by the irreversibility of well-known phenomena. Mechanics could not explain the temporal direction of natural processes, because "the processes of rational Mechanics can both follow and go back up the course of time". He thought that mechanical models could be easily skipped in favour of some kind of direct approach to experience, which would have allowed us "to see directly" the world, without "any picture, any symbol". It seems a very naïve point of view: no physical theory can avoid some kind of "symbols" or representations. In reality, Ostwald intended something definitely less dramatic: science had to confine itself to quantitative relationships among "entities which could be handled and measured". The most important of these entities was "the most general invariant, energy", or better, any difference of energy.[24]

Energy assumed the role previously played by matter. According to Ostwald, matter was "a mental creation" put forward in order to "represent what is constant in transformations", whereas the material

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"unumkehrbar" in the subsequent editions of his treatise on Thermodynamics, namely *Vorlesungen über Thermodynamik* (first edition 1897), see Uffink J. 2001, pp. 343-58.

[23] Ostwald W. 1895a, p. 953-5.

[24] Ostwald W. 1895a, p. 955-7.

effects of those transformations on our senses depended on energy. The concept of energy could explain "what had been explained by means of the entities matter and force, and even more". Forces, "whose existence we cannot demonstrate", were assumed to act on atoms, "which we cannot see". They had to be replaced by "the quantities of energy at stake in the phenomenon under consideration". The conceptual and mathematical framework for every kind of phenomena required the specification of space, time and energy. Ostwald's passionate hymn to energy was accompanied by a more sober meta-theoretical attitude towards scientific practice. He quoted Kirchhoff and his preference for "the description of facts" rather than "the explanation of Nature". This phenomenological attitude stood beside an evolutionary conception of science: "the advantages of the energetic theory over the mechanical theory" notwithstanding, energetics was not to be looked upon as the final stage of science. In an unspecified future, Ostwald expected a wider-scope theory, wherein energetics would have appeared as "a specific instance of more general relations". He was "loath to fix" any a-priori "boundary to the progress of science".[25]

When we compare Ostwald's *energetics* to Duhem's *energetics*, we find a remarkable difference: the unifying power of very general mathematical structures in the latter, and the unifying power of a specific physical entity in the former. Moreover, Ostwald's phenomenology appears quite naïve when compared to Duhem's appreciation for the structural analogies between different fields of science. Indeed, formal or structural analogies were the keystone of Duhem's design of unification, where Analytical Mechanics, Thermodynamics and Chemistry could find a natural re-interpretation. In the passage from Analytical Mechanics to Thermodynamics, the mathematical structures underwent a generalisation, but a further generalisation was re-

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[25] Ostwald W. 1895a, pp. 957-8. In a brief letter Ostwald sent to the same journal after some weeks as a response to the criticism of the French physicist Marcel Brillouin, he stressed synthetically the same view put forward in the previous paper. With regard to the meta-theoretical level, he insisted on his radical phenomenology: energetics dealt with mathematical symbols which expressed "*nothing else but the facts to be represented*". With regard to the theoretical level, he reminded the reader that, after having spent ten years "in building up a mechanical theory of chemical affinities", he had decided to "give up looking for any mechanical analogy". (See Ostwald W. 1895b, pp. 1070-1)

quired in order to tame other phenomena of increasing complexity. Just after the publication of his *Introduction à la mécanique chimique*, Duhem started to mathematically tame irreversible or permanent deformations which emerged from mechanical and magnetic hysteresis.

In 1894 Duhem sent a long paper under the title *Sur les déformations permanentes et l'hystérésis* to a Belgian scientific journal. The following year he sent two other papers under the same title, but with the subtitles Les *modifications permanentes du soufre*, and *Théorie générale des modifications permanentes*. In 1896, L'*Académie Royale de Belgique* published the three papers in the same volume as a series of *Première Mémoire, Deuxième Mémoire*, and *Troisième Mémoire*. The first paper begins with a short historical account of "infrequent" attempts at "making the different kinds of permanent deformations match with the principles of thermodynamics". According to Duhem, the difficulties in coping with permanent deformations stemmed from "the restrictive hypothesis" which preceded "the demonstration of Carnot's theorem" or the second Principle of thermodynamics. The hypothesis assumed the existence of "*reversible transformations*" or transformations which could be looked upon as "*a continuous series of states of equilibrium*". The restriction to reversible transformations obviously excluded phenomena like magnetic hysteresis: as Duhem remarked, in this kind of phenomena, "*a continuous series of states of equilibrium is not a reversible transformation*". The second Principle of thermodynamics could not be called into play: only "the principle of equivalence between heat and work", namely the first Principle of Thermodynamics, was at stake.[26]

Duhem started from a simplified physical system defined by a temperature T and a single "normal variable x", and applied to it "the classic propositions of thermodynamics". Among them, the first Principle, the definition of internal thermodynamic potential, the relationship between internal energy and internal potential, and the condition of equilibrium under an external force X: $X = \partial \mathsf{F}(x,T)/\partial x$. If the differentiation of the external force required in general that

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[26] Duhem P. 1894b, pp. 3 and 7. In this case the Belgian scientific journal was *Mémoires présentés par Divers Savants Etrangers et Mémoirs couronnés par l'Académie Royale de Belgique*.

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

a more general expression

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

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

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

split into two equations, according to $dx > 0$ or $dx < 0$ in the course of the transformation.

$$\frac{dX}{dx} = \frac{\partial^2 \mathsf{F}\,(x,T)}{\partial x^2} + f(x,T,X) \text{ and } \frac{dX}{dx} = \frac{\partial^2 \mathsf{F}\,(x,T)}{\partial x^2} - f(x,T,X).$$[27]

The two equations gave rise to a "family of ascending" and "descending curves": Duhem assumed the existence of a new kind of closed cycle, a cycle of hysteresis, which consisted of "a descending curve and an ascending curve meeting at two points". This was "the most simple closed cycle we can conceive", namely "*a simple closed cycle*": every closed cycle had to be composed of whatsoever number of simple cycles. The new kind of cycle was, in some way, the fundamental entity of the new thermodynamics of permanent, irreversible

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[27] Duhem P. 1894b, pp. 7-10.

transformations. When a force dX was applied to the physical system, and then applied in the opposite direction, the vectorial sum of forces vanished, but the sum of the corresponding strains dx_1 and dx_2 did not. According to the simplified equation,

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

$$\sum_{k=1}^{2} dx_k = -\frac{f(x,T,X)}{\dfrac{\partial^2 F\,(x,T)}{\partial x^2}}\sum_{k=1}^{2}|dx_k|.$$[28]

The physical system did not return to its initial conditions: it experienced an irreversible strain. Only if $f(x,T,X)=0$, the system could avoid an irreversible transformation: in this case the system maintained what Duhem labelled its "natural states".

> Cette égalité (16) nous montre que $(x_1 - x_0)$ n'est pas nul en général. *Lorsqu'à la fin d'une modification isothermique infiniment petite, l'action extérieure reprend sa valeur primitive, la variable normale x ne reprend pas sa valeur primitive, la variable normale x ne reprend pas sa valeur primitive ; elle éprouve une variation permanente.*
>
> Il y a exception à cette règle dans le cas où
>
> $$f(x,T,X)=0.$$
>
> Dans ce cas, l'égalité (16) devient
>
> $$x_1 - x_0 = 0.$$
>
> *Une modification infiniment petite, accomplie au voisinage d'un état naturel, n'entraine aucune modification permanente*. Si donc on n'étudie que des modifications très petite autour d'un état naturel du système, on pourra leur appliquer les lois ordinaires de la thermodynamique ; …[29]

After a series of long mathematical steps, Duhem showed the existence of two kinds of permanent deformations, corresponding to two slightly different cycles. In spite of the very slight difference in their geometrical representations, systems of the "first" and of the "second

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[28] Duhem P. 1894b, pp. 11, 13, and 17. I have slightly modified Duhem's formalism in order to make it clearer.

[29] Duhem P. 1894b, pp. 17-8.

category" behaved in a very different way with regard to stability. After other mathematical steps (and some misprints) Duhem found that the first kind of systems approached "*the natural state* $(\xi, X_{0,} T_0)$ *corresponding to the temperature* T_0 *and the external action* X_0". The systems were therefore stable. On the contrary, systems of the second kind were not stable: they changed "endlessly" when submitted to "*an external force and a temperature* THEREABOUTS *constant*". This difference involved even "natural states": they were "*stable states for systems of the first category*" but "*instable states for the systems of the second category*".[30]

Duhem made use of the non-simplified equation in order to describe simple mechanical systems: "a homogeneous cylinder submitted to a traction", or "torsion", or "flexion". All these instances of "very simple and marked permanent deformations" would correspond to systems of the "*second category*". The other kind of permanent deformations belonging to the "*first category*" corresponded to processes like quenching. If traction, torsion and flexion represented the mechanical side, quenching represented the thermal side of Duhem's theory of permanent deformations. If elastic deformations could be mathematically represented in an abstract *plane* (X, x), thermal processes like quenching could suitably be represented in an abstract *plane* (T, x).[31]

A slightly different approach was required in the case of magnetic permanent deformations, namely the phenomena known as "magnetic hysteresis", because the concept of "*external action*" did not suit "a magnetic element placed inside a magnet". Differently from the mechanical case, there were two kinds of "magnetism": if the magnetic action $\boldsymbol{H}$ could be derived from a "potential function V ", the "state of magnetisation" M stood in a *recursive* relationship with $\boldsymbol{H}$. In the specific case of "perfectly *soft* bodies", $\mathrm{M} = F(\mathrm{M}, T)H$ played the role of a "normal variable", where the function $F(\mathrm{M}, T)$ was "the magnetising function". Both $\boldsymbol{H}$ and M were submitted to other specific "restrictions", and Duhem acknowledged that his mathematical model was "very specific": he looked upon it as "a first step towards the general theory of magnetic hysteresis". The action $\boldsymbol{H}$ was assumed

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[30] Duhem P. 1894b, pp. 33-4 and 37-8.

[31] Duhem P. 1894b, pp. 38 and 44-5.

to have "a constant direction", and the magnetisation M was supposed to act in the same direction as ***H***: these restrictions allowed Duhem to make use of a scalar rather than vector "normal variable". The formal analogy between mechanical and magnetic processes led Duhem to marshal a series of mathematical steps leading to his "*fundamental equation of magnetic hysteresis*":

$$dH = G(\mathrm{M},T)d\mathrm{M} + g(\mathrm{M},T)dT + f(\mathrm{M},H,T)|d\mathrm{M}|.$$

In this case, Duhem did not pursue his usual physical-mathematical approach in terms of internal thermodynamic potential. It was "the experience" to show that "a magnetised body is a system of the first category". He was aware of the tentative and provisional nature of his theory: a more general theory, based "on more than one normal variable", was waiting to be built up.[32]

The second paper which Duhem devoted to permanent deformations dealt with quite a specific chemical-physical phenomenon: "the permanent modifications experienced by sulphur under the influence of heat". Duhem was facing phenomena placed outside the scope of ordinary mechanics, thermodynamics and chemistry. He saw an analogy between the change of the physical state of sulphur and the process of quenching: both of them were transformations occurring "at variable temperature under a constant external action". In his mathematical toolbox he introduced two "normal parameters" in addition to temperature T: the volume v of the system and "a third variable x, whose nature will be left unspecified at the moment". A "normal and uniform pressure" Π was the external force" corresponding to the parameter v: it was indeed the sole force which the system experienced. A very general equation described that kind of permanent transformations:

$$\frac{\partial^2 \mathsf{F}\,(x,v,T)}{\partial x\,\partial v}\delta v + \frac{\partial^2 \mathsf{F}\,(x,v,T)}{\partial x\,\partial T}\delta T + \frac{\partial^2 \mathsf{F}\,(x,v,T)}{\partial^2 x}\delta x + f(x,v,\Pi,T)|\delta x| = 0.$$[33]

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[32] Duhem P. 1894b, pp. 51-3, 59, and 61.

[33] Duhem P. 1895a, pp. 4-5 and 8-9.

The legacy of "ascending", "descending" and "natural" curves, as well as first- and second-category closed cycles, were transferred unchanged in the new kind of physical-chemical permanent transformation. The physical and geometrical approach became more sophisticated, since Duhem took into account "endothermic" and "exothermal" transformations, and a new sub-division into "clockwise" and "anticlockwise" transformations. At the end he displayed eight families of closed cycles, according to three binary parameters: the "category", the direction of the path, and the sign of exchanged heat. Duhem showed that, if "Clausius' inequality" $\int dQ/T > 0$ had been assumed as a further hypothesis, the eight families of closed cycles would have become four.[34]

In the third paper, he briefly recollected the specific processes he had studied in the first two papers: mechanical deformations, magnetic hysteresis, quenching, and sulphur transformations. Then he stressed the necessity of "a more general point of view", which could encompass systems described "by any number of normal parameters", and simultaneous variations of temperature and external actions. Moreover, such a mathematical generalisation had to be integrated with the theory he had put forward in his *Commentaire aux principes de la thermodynamique*.[35] The thermodynamics of reversible processes had a too narrow scope, and processes of permanent deformations called into play "a wider, more comprehensive thermodynamics". In the set of Lagrangian parameters $\alpha, \beta, \ldots\ldots, \nu$ Duhem defined two subsets $\alpha, \beta, \ldots\ldots, \lambda$ and $\mu, \ldots\ldots, \nu$. To the second subset he associated a series of *old* (necessary but not sufficient) conditions of equilibrium

$$M = \frac{\partial \mathsf{F}}{\partial \mu} \quad or \quad dM = \frac{\partial^2 \mathsf{F}}{\partial \alpha\, \partial \mu} d\alpha + \ldots + \frac{\partial^2 \mathsf{F}}{\partial^2 \mu} d\mu + \ldots + \frac{\partial^2 \mathsf{F}}{\partial \nu\, \partial \mu} d\nu$$

……

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[34] Duhem P. 1895a, pp. 27, 33 and 35-6. In particular, endothermic cycles could only be clockwise, and exothermal ones only anticlockwise. As Duhem remarked, an irreversible cycle does not fulfil the conditions required by the demonstration of "Clausius' inequality". (See *Ibidem*, p. 35)

[35] Duhem P. 1895b, p. 4.

$$N=\frac{\partial \mathsf{F}}{\partial \nu} \quad or \quad dN=\frac{\partial^2 \mathsf{F}}{\partial \alpha\, \partial \nu}d\alpha+\ldots+\frac{\partial^2 \mathsf{F}}{\partial \mu \partial \nu}d\mu+\ldots+\frac{\partial^2 \mathsf{F}}{\partial^2 \nu}d\nu,$$

whereas to the first subset of parameters he associated a series of *new* conditions

$$dA=\frac{\partial^2 \mathsf{F}}{\partial \alpha^2}d\alpha+\ldots+\frac{\partial^2 \mathsf{F}}{\partial \lambda\, \partial \alpha}d\lambda+\frac{\partial^2 \mathsf{F}}{\partial \mu \partial \alpha}d\mu+\ldots+\frac{\partial^2 \mathsf{F}}{\partial \nu\, \partial \alpha}d\nu+\frac{\partial^2 \mathsf{F}}{\partial T\, \partial \alpha}dT+g_\alpha(\alpha,\ldots,\nu,T)|d\alpha|$$

……

$$dL=\frac{\partial^2 \mathsf{F}}{\partial \alpha\, \partial \lambda}d\alpha+\ldots+\frac{\partial^2 \mathsf{F}}{\partial \lambda^2}d\lambda+\frac{\partial^2 \mathsf{F}}{\partial \mu \partial \lambda}d\mu+\ldots+\frac{\partial^2 \mathsf{F}}{\partial \nu \partial \lambda}d\nu+\frac{\partial^2 \mathsf{F}}{\partial T\, \partial \lambda}dT+g_\lambda(\alpha,\ldots,\nu,T)|d\lambda|$$

.

Only these parameters were affected by irreversible effects. With regard to the function $\mathsf{F}\,(\alpha,\beta,\ldots\ldots,\nu,T)$, he specified that its existence depended on the choice of the parameters $\alpha,\beta,\ldots\ldots,\nu$: for the moment he confined himself to state that they had to be "CONVENIENTLY CHOSEN".[36]

A very delicate issue concerned the choice of parameters: the structure of the last set of equations was not invariant under a general transformation of parameters. Only a transformation less general, which did not mix the two subsets of parameters, could save the invariance of the equations. If the mathematical description of the physical system was sensitive to the choice of the parameters, there was a sort of mathematical *instability* of the equations. Nevertheless

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[36] Duhem P. 1895b, pp. 8-9. The physical and logical relationship between the new and old theory, as well as the mathematical difficulty associated with the existence of the function $\mathsf{F}\,(\alpha,\beta,\ldots\ldots,\nu,T)$ was briefly clarified in the following pages. The introduction of two subsets of parameters assured formally that "the theory deduced from the new hypothesis contains the old thermodynamics": the reduction of the new to the old theory took place when the system did not depend on the subset of Lagrangian parameters $\alpha,\beta,\ldots\ldots,\lambda$. Nevertheless, physical and logical objections could be raised against that reduction: the two theories were "in general, incompatible", for they were based on the incompatible hypotheses of reversibility and irreversibility, even though "the new hypothesis gives rise to the old hypothesis in this specific case". The logical incompatibility could only be removed by a sort of logical somersault leading one to look upon reversibility as a specific instance of irreversibility.

Duhem went on with other generalisations. Duhem imagined "an infinitely small transformation" which led "the temperature *T* and the external forces *A*, *B*, …, *N*" to regain "their initial values". If $\alpha_0,\beta_0,\ldots\ldots,\nu_0$ were the initial values of the parameters, their final values $\alpha_1,\beta_1,\ldots\ldots,\nu_1$ were generally different from $\alpha_0,\beta_0,\ldots\ldots,\nu_0$.[37] The infinitesimal character of the transformation allowed him to perform an approximate integration of differential equations:

$$
\begin{aligned}
&\frac{\partial^2 F}{\partial\alpha^2}(\alpha_1-\alpha_0)+\ldots\ldots+\frac{\partial^2 F}{\partial\nu\,\partial\alpha}(\nu_1-\nu_0)+g_\alpha\int|d\alpha|=0\\
&\ldots\ldots\\
&\frac{\partial^2 F}{\partial\alpha\,\partial\lambda}(\alpha_1-\alpha_0)+\ldots\ldots+\frac{\partial^2 F}{\partial\nu\,\partial\lambda}(\nu_1-\nu_0)+g_\lambda\int|d\lambda|=0\\
&\frac{\partial^2 F}{\partial\alpha\,\partial\mu}(\alpha_1-\alpha_0)+\ldots\ldots+\frac{\partial^2 F}{\partial\nu\,\partial\mu}(\nu_1-\nu_0)=0\\
&\ldots\ldots\\
&\frac{\partial^2 F}{\partial\alpha\,\partial\nu}(\alpha_1-\alpha_0)+\ldots\ldots+\frac{\partial^2 F}{\partial^2\nu}(\nu_1-\nu_0)=0.
\end{aligned}
$$

From the mathematical point of view, the functions $g_\alpha,g_\beta,\ldots,g_\lambda$ prevented the system of equations from becoming a homogeneous system. Only if some functions $g_\alpha,g_\beta,\ldots,g_\lambda$ do not vanish, the system yields non-vanishing solutions for the set of deformations $(\alpha_1-\alpha_0),\ldots\ldots,(\nu_1-\nu_0)$: in this case, the physical system experiences permanent deformations.[38]

At the end of his third paper on permanent deformations, in the short "Conclusion", Duhem remarked that he had shown a mere possibility: he had outlined a provisional mathematical theory, which depended on various specific conditions. The theory could "cast some light" on a very demanding subject matter, but raised many questions.[39]. He went on to publish four other papers on the same subject,

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[37] Duhem 1895b, pp. 11-2 and 22.

[38] Duhem 1895b, p. 23. When $g_\alpha=g_\beta=\ldots\ldots=g_\lambda=0$, the mathematical system becomes homogeneous, and yields the trivial solution $(\alpha_1-\alpha_0)=\ldots\ldots=(\nu_1-\nu_0)=0$.

[39] See Duhem 1895b, pp. 54-5: "La présente étude montre que l'on peut énoncer, pour les états naturels qui sont stables, des propositions semblables de tout point à celles dont les

and under the same title *Sur les déformations permanentes et l'hystérésis*, until 1901. At the same time, he continued to develop the formal structure of his *Energetics* or generalised Mechanics. The long essay he published in 1896 represented a further effort of generalisation: it is the subject of the next chapters.

états d'équilibre stable des systèmes dépourvus de modifications permanentes sont, depuis longtemps, l'objet. Il nous semble qu'elle jette par là un jour nouveau sur les relations qui existent entre la thermodynamique classique et la théorie des déformations permanentes, telle que nous l'avons exposée dans les deux précédentes publications."

9. 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.[1]

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 ex-

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[1] 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.

pected to behave in the opposite way. Nevertheless the law seemed "in opposition to a huge number of specific instances".[2]

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 da 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 nécessairement d'un état à un autre, il arrive souvent que la modification annoncée ne se réalise pas.*[3]

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 $\alpha, \beta, \ldots, \lambda$, is kept in equilibrium by "*external actions*" A, B, …, L, which "*are specified, **without any am-***

---

[2] 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.

[3] Duhem P. 1896a, p. 5.

***biguity** in terms of α, β, …, λ and T"*. When we invert the mathematical system, we find the set the set of values for parameters α, β, …, and λ 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*, …, *L*":

$$\begin{array}{ll} A = f_\alpha(\alpha,\beta,.....,\lambda,T), & \alpha = h_\alpha(A,B,.....,L,T) \\ B = f_\beta(\alpha,\beta,.....,\lambda,T) & \beta = h_\beta(A,B,.....,L,T) \\ \ldots\ldots & \ldots\ldots \\ L = f_\lambda(\alpha,\beta,.....,\lambda,T), & \lambda = h_\lambda(A,B,.....,L,T) \end{array}$$

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".[4]

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:

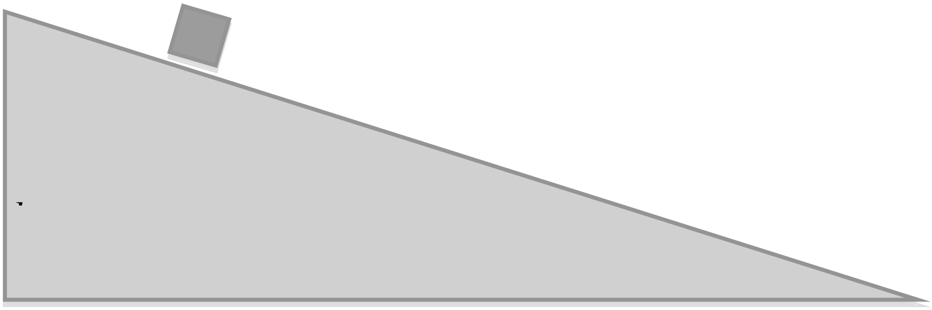
> *Toutes les fois que la* mécanique *classique, où l'on fait abstraction du frottement, fait prévoir qu'un état du système étudié est un état d'équilibre,*

---

[4] 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*."

> *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.*[5]

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 α 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 α 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:

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[5] Duhem 1896a, p. 8.

$f\,m\,g\cos\alpha \geq m\,g\sin\alpha$ or $tg\alpha \leq f$.[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".[7]

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

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[6] 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.*"

[7] Duhem P. 1896a, pp. 9-11.

"delays in boiling", "delays in condensation", "oversaturation in gaseous solutions", and *"delays in decompositions"*.[8]

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.[9]

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

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[8] Duhem P. 1896a, pp. 12-13.

[9] Duhem P. 1896a, pp. 14-5.

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 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.[10]

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" $\alpha,\beta,......,\lambda$. In the mathematical-physical toolbox, Duhem put the living force T of the system as a whole, the internal thermodynamic potential $\mathrm{F}\left(\alpha,\beta,......,\lambda,T\right)$, and the external forces *A, B, …, L*. To those basic functions he added the "*passive resistances*" or "*viscous resistances*" $f_\alpha,f_\beta,......,f_\lambda$, depending on the parameters $\alpha,\beta,......,\lambda,T$ and their time derivatives $\alpha'=\frac{d\alpha}{dt},\beta'=\frac{d\beta}{dt},......,\lambda'=\frac{d\lambda}{dt}$. As Duhem remarked, the work done by the "resistances"

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

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

---

[10] 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.

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

……

$$L+\frac{\partial \mathcal{T}}{\partial \lambda}-\frac{d}{dt}\frac{\partial \mathcal{T}}{\partial \lambda'}-\frac{\partial \mathcal{F}}{\partial \lambda}+f_{\lambda}=0.$$[11]

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

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

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

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

had been updated in 1894:

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

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

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

……

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

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[11] Duhem P. 1896a, pp. 20-1.

[12] 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, Θ. Afterwards, in the next sections of the paper, he confined himself to a simpler case, where the variation of ϑ did not affect the other parameters, and $\Theta=f_{\vartheta}=0$. Moreover he chose $\vartheta=T$.

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

$$dQ = -\left(+T\frac{\partial S}{\partial \alpha}d\alpha + \frac{f_\alpha}{E}d\alpha + \ldots\ldots + T\frac{\partial S}{\partial \lambda}d\lambda + \frac{f_\lambda}{E}d\lambda \right) =$$
$$= -T\,dS - \frac{1}{E}\left(f_\alpha\frac{d\alpha}{dt} + f_\beta\frac{d\beta}{dt} + \ldots\ldots + f_\lambda\frac{d\lambda}{dt} \right)dt.$$

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

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

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

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

In the second generalisation, Duhem assumed that the system was composed of two parts "independent of each other", although interacting in some way. The internal energy and the internal thermodynamic potential of each part considered in itself were labelled Y_1 and Y_2, and F_1 and F_2. Internal energy and thermodynamic potential of the whole system could not be the mere sum of the two functions, but required a *potential of interaction* Ψ.

Duhem put forward a sort of geometrisation of the interaction between the two subsets of the physical system. He imagined a series of links or *bonds* expressed by a series of equations of the kind

$$\begin{array}{l} (\,M_1\,\delta\alpha_1 + \ldots\ldots + P_1\,\delta\lambda_1 + M_2\,\delta\alpha_2 + \ldots\ldots + P_2\,\delta\lambda_2 = 0 \\ M'_1\,\delta\alpha_1 + \ldots\ldots + P'_1\,\delta\lambda_1 + M'_2\,\delta\alpha_2 + \ldots\ldots + P'_2\,\delta\lambda_2 = 0 \\ \ldots\ldots\ \ldots\ldots \end{array} .$$

---

[13] Duhem P. 1896a, p. 23.

He imagined a hierarchy of bonds which were activated one after the other when the two subsets approached each other. Every bond, when activated, triggered off a new kind of "viscous resistance", and a new term appeared in the equations of motion. There was a hierarchy of "viscosities", which corresponded to a series of waste of energy.[14]

The negative sign of the "work done by viscous forces" led to

$$dQ \geq -T_1\, dS_1 - T_2\, dS_2,$$

in accordance with the second Principle of Thermodynamics. The result could be extended to a system composed of q rather than 2 parts:

$$dQ \geq -T_1\, dS_1 - T_2\, dS_2 - \ldots\ldots - T_q\, dS_q .$$

In the specific case of an isolated system, $dQ = 0$, and the previous inequality yielded the new inequality

$$T_1\, dS_1 + T_2\, dS_2 + \ldots\ldots + T_q\, dS_q \geq 0 ,$$

which Duhem looked upon as a "*generalisation*" of Clausius' statement on the variation of entropy in "*an isolated system whose points have the same temperature*".[15]

At this point, he put forward a further generalisation, and took into account a system which was not isolated from "external bodies". Duhem found no formal differences in the "equations of motion" between this system and the previous one, but in this case he had "no information" about the mathematical sign of the *viscous* work. Differently from an isolated system, wherein the fluxes of energy are submitted to definite conditions, a physical system in interaction with an

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[14] Duhem P. 1896a, pp. 24-6 and 28-9. In order to specify the links or bonds acting between the subsets, Duhem made use of the word "*soudure*" besides "liaison" and "contact". The fact is that, in Duhem's new theory, the word "viscosity" had a wide meaning and a corresponding wide scope.

[15] Duhem P. 1896a, pp. 33-6. In the text there are some misprints in equations and inequalities involving dQ.

environment could give and receive energy in many different ways. The variation of entropy of an open system was unpredictable.

> Ainsi, *lorsqu'un système de température uniforme présente avec les corps extérieurs des liaisons bilatérales, il n'est plus juste de dire, en général, que la transformation compensée* $\left(-E\,dS_1/dt\right)dt$ *qui accompagne une modification réelle de ce système ne peut surpasser la valeur totale de transformation* dQ_1/T_1 *; la transformation non compensée peut être négative.*
>
> En intégrant l'équation (37) pour un cycle fermé, on parvient à la proposition suivante :
>
> L*orsqu'un système, de température à chaque instant uniforme, qui présente avec les corps extérieures des liaison bilatérales, parcourt un cycle fermé réel, il peut se faire que l'intégrale* $\int dQ_1/T_1$*, étendue à ce cycle, ait une valeur négative.*
>
> Les théorèmes célèbres de R. Clausius pourraient donc conduire à des résultats erronés si on les appliquait à un système tel que celui qui nous occupe ; …[16]

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

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

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

$$
\begin{aligned}
&A,B,\ldots\ldots,L\rightarrow \mathrm{A}\ ,\mathrm{B}\ ,\ldots\ldots,\mathrm{L}\\
&\frac{\partial \mathrm{F}}{\partial\alpha},\frac{\partial \mathrm{F}}{\partial\beta},\ldots\ldots,\frac{\partial \mathrm{F}}{\partial\lambda}\rightarrow\Phi_a,\Phi_b,\ldots\ldots,\Phi_l\\
&f_\alpha,f_\beta,\ldots\ldots,f_\lambda\rightarrow\varphi_\alpha,\varphi_\beta,\ldots\ldots,\varphi_\lambda
\end{aligned}
$$

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[16] Duhem 1896a, pp. 44-5. There are also some misprints in these pages, Duhem's plus/minus dysgraphie included.

$$\frac{\partial \mathrm{T}}{\partial \alpha}-\frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \alpha'},\ \frac{\partial \mathrm{T}}{\partial \beta}-\frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \beta'},\ldots\ldots,\ \frac{\partial \mathrm{T}}{\partial \lambda}-\frac{d}{dt}\frac{\partial \mathrm{T}}{\partial \lambda'} \to J_a, J_b, \ldots\ldots, J_l.$$

Therefore the equations of motion were formally expressed by the equations

$$\begin{gathered}\mathrm{A}-\Phi_a+J_a+\varphi_a=0 \\ \mathrm{B}-\Phi_b+J_b+\varphi_b=0 \\ \ldots\ldots \\ \mathrm{L}-\Phi_l+J_l+\varphi_l=0.\end{gathered}$$[17]

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

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

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

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[17] Duhem P. 1896a, pp. 67-8 and 70-2.

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

was negative.[18]

Only at this stage Duhem explained the physical meaning of the linear mathematical transformation on the Lagrangian parameters $\alpha, \beta, \ldots\ldots, \lambda$. The new set $a, b, \ldots\ldots, l$ 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* $\delta a, \delta b, \ldots\ldots, \delta l$*, données par les égalités (82), il en est six* $\delta m, \ldots\ldots, \delta n$ *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* $g_a, g_b, \ldots\ldots, g_l$ *qui leur correspondent sont identiquement nulles.*[19]

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*
>
> $$\begin{cases} \gamma_a \leq \mathrm{A} - \Phi_a \leq -\gamma_a \\ \gamma_b \leq \mathrm{B} - \Phi_b \leq -\gamma_b \\ \ldots\ldots \\ \gamma_l \leq \mathrm{L} - \Phi_l \leq -\gamma_l \end{cases} \quad \text{and} \quad \begin{cases} \mathrm{M} - \Phi_m = 0 \\ \ldots\ldots \\ \mathrm{N} - \Phi_n = 0 \end{cases} .^{20}$$

---

[18] Duhem 1896a, pp. 72-5.

[19] Duhem 1896a, p. 74.

[20] Duhem P. 1896a, p. 77.

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":

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

.

> 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.*[21]

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.

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[21] Duhem 1896a, pp. 83-4. A misleading misprint appears in the equation above the quotation.

10. THE RE-EMERGENCE OF AN ANCIENT TRADITION

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. He imagined a system composed of two parts with "masses" M_1 and M_2; he chose as "normal" parameters T, $\alpha,\beta,\ldots\ldots,\lambda$, and v_1,v_2, the "specific volumes" of the two masses. He assumed that, in general, M_1 and M_2 could depend on $\alpha,\beta,\ldots\ldots,\lambda$. The only external action acting on the system was "a normal and uniform pressure P". The volume V of the system could be expressed in terms of the two parameters v_1,v_2: $V=V_1+V_1=M_1\,v_1+M_2\,v_2$.

The equations corresponding to $\alpha,\beta,\ldots\ldots,\lambda$ did not contain "inertial" terms:

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

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

$$\ldots\ldots$$

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

Duhem assumed that "viscosity and friction" corresponding to the parameters v_1,v_2 could be disregarded, and "inertial force" could also be neglected. He expressed the equation of motion for the parameters v_1,v_2 in accordance with the old mathematical representation:

$$PM_1 + \frac{\partial \mathrm{F}}{\partial v_1} = 0$$
$$PM_2 + \frac{\partial \mathrm{F}}{\partial v_2} = 0.$$[1]

At this point Duhem called into play the thermodynamic potential $H = \mathrm{F} + PV$, 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:

$$\frac{\partial H}{\partial \alpha}, \frac{\partial H}{\partial \beta}, \ldots\ldots, \frac{\partial H}{\partial \lambda} \to \eta_a, \eta_b, \ldots\ldots, \eta_l,$$

he showed the physical soundness of the typographic simplification

$$\eta_a = -\mathrm{A} + \Phi_a$$
$$\ldots\ldots$$
$$\eta_l = -\mathrm{L} + \Phi_l,$$

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

$$\eta_a - \varphi_a - g_a \frac{a'}{|a'|} = 0$$
$$\ldots\ldots$$
$$\eta_l - \varphi_l - g_l \frac{l'}{|l'|} = 0.$$[2]

These equations contained three kinds of terms: if the first corresponded to the derivatives of a thermodynamic potential, the other

---

[1] 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, 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.

[2] Duhem P. 1896a, pp. 92-3. Duhem's potential H corresponded to Massieu's potential H' and Gibb's potential ζ.

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 $\varphi_\alpha, \varphi_\beta, \ldots\ldots, \varphi_\lambda$ and $g_a, g_b, \ldots\ldots, g_l$. In the last section of the chapter, Duhem outlined a similar mathematical procedure for the set of Lagrangian parameters $\alpha, \beta, \ldots\ldots, \lambda$, T, V, instead of $\alpha, \beta, \ldots\ldots, \lambda$, T, P.[3]

However he confined himself to systems described by only one Lagrangian parameter α, apart from "a uniform and constant pressure P" and "a variable temperature T". 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,α), which corresponded to "the curve of true equilibrium" under constant pressure P. In general, friction did exist, and the condition of equilibrium for the system

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[3] 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.

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,α) corresponded to the equations

$$\frac{\partial H(P,\alpha,T)}{\partial \alpha} + \gamma(P,\alpha,T) = 0 \quad \text{and} \quad \frac{\partial H(P,\alpha,T)}{\partial \alpha} - \gamma(P,\alpha,T) = 0.$$[4]

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 α constitue un changement d'état chimique, les deux fonctions positives*
>
> $$-\gamma(P,\alpha,T),$$
> $$-\Gamma(V,\alpha,T)$$
>
> *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.*[5]

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 thermody-

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[4] Duhem P. 1896a, pp. 99-101.

[5] Duhem P. 1896a, p. 104.

namics 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 thermochemical 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.[6]

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,α) 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, α 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 particular, that the

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[6] Duhem P. 1896a, p. 105.

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

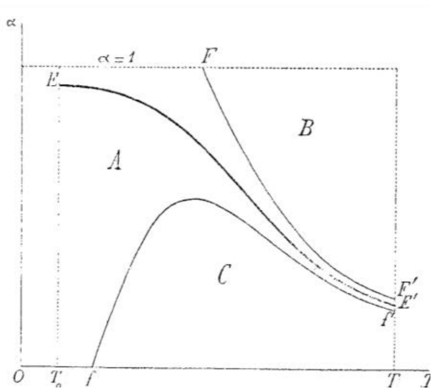

Figure 1 (Duhem P. 1896a, p. 106)

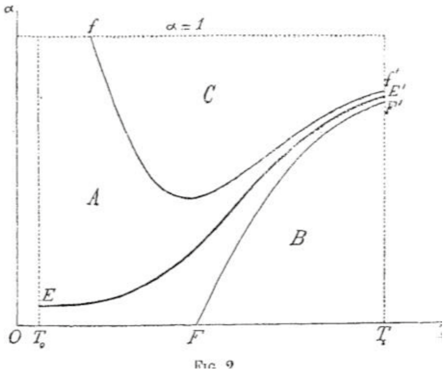

Figure 2 (Duhem P. 1896a, p. 107)

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 α atteigne la valeur α_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 α soit réduit à la valeur α_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.[7]

The same kind of considerations were suitable for endothermic processes taking place at constant volume, as well as for both exothermic and

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[7] Duhem P. 1896a, pp. 106-7.

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, 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 ϑ the temperature corresponding to this intersection: if we increase the temperature of the system beyond ϑ, the system will undergo a combination or decomposition.

> Nous pouvons donc énoncer les théorèmes suivants :
>
> *Un système, pris avec une composition initiale donnée* α*, 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* α*, 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.*[8]

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 α", while $\Theta(\alpha,P)$ was "the point of reaction under constant pressure P". The point of reaction depended obviously "on the initial composition α of

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[8] Duhem P. 1896a, p. 109.

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.[9]

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

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

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

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

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

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

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[9] 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.

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

$$\frac{\partial H(P,\alpha,T)}{\partial\alpha}-\gamma(P,\alpha,T)-\Phi(P,\alpha,T)\cdot\alpha'=0,$$
$$\frac{\partial H(P,\alpha,T)}{\partial\alpha}+\gamma(P,\alpha,T)-\Phi(P,\alpha,T)\cdot\alpha'=0.$$ [10]

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

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

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

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

The denominator decreased when "viscosity" decreased, namely when the system approached classic thermodynamic behaviour.[11]

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.

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[10] Duhem P. 1896a, p. 128.

[11] Duhem P. 1896a, pp. 129 and 131. There are some plus/minus misprints in Duhem's equations.

> 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.*[12]

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 α et dont la force vive varie avec α, 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.*[13]

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

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[12] Duhem 1896a, p. 131. Duhem's previous hypothesis on the behaviour of these systems relative to the temperature can be found on page 104.

[13] Duhem 1896a, p. 130.

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 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.[14]

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

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[14] Duhem P. 1896a, pp. 130-1.

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.[15]

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.

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.

In the last two chapters of his 1896 book, Duhem tried to cope with two phenomena to be found at the opposite ends of his broad-spectrum physics: explosive reactions in chemistry, and dissipative effects in purely mechanical motions. In the first case, he started from the study of stability in chemical systems and wondered whether states corresponding to the "*limiting state of false equilibrium*", defined by the equations

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[15] 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.

$$\frac{\partial H(P,\alpha,T)}{\partial \alpha}+\gamma(P,\alpha,T)=0 \quad \text{or} \quad (170'') \ \frac{\partial H(P,\alpha,T)}{\partial \alpha}-\gamma(P,\alpha,T)=0,$$

were "stable" or "indifferent" states. He analysed two kinds of transformation, isothermal and adiabatic, and concluded that, in isothermal transformations, "*every limiting state of false equilibrium is stable or indifferent*", while in adiabatic transformations, the situation was more complex and "interesting".[16]

Then he followed "another pathway". He tried to estimate "*the acceleration of the reaction*": a positive "acceleration" entailed a velocity of reaction continuously increasing, and therefore an explosive reaction. The synthetic equation

$$\frac{d\alpha}{dt}=\frac{\dfrac{\partial H(P,\alpha,T)}{\partial \alpha}-\gamma(P,\alpha,T)\dfrac{\alpha'}{|\alpha'|}}{\Phi(P,\alpha,T)},$$

became the starting point for the computation of the acceleration. After the time-derivation, and another series of demanding computations, Duhem was able to show that

> *Au voisinage d'un faux équilibre limite stable, le système est le siège d'une réaction modérée : au voisinage d'un faux équilibre limite instable, le système est le siège d'une explosion.*[17]

When Duhem tried to extend his inquiry to states represented by points far from the region of false equilibrium, the theory became more phenomenological. He made recourse to other hypotheses, and tuned the results of the theory with the available experimental results. He found that, in exothermic reactions, the region of combination split into two complementary sub-regions. The upper side, closer to the region of false equilibria, was the seat of "mild" reactions, while the lower side was the seat of "explosive" reactions.[18]

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[16] Duhem P. 1896a, pp. 139-40 and 142.

[17] Duhem P. 1896a, p. 155.

[18] Duhem P. 1896a, p. 163.

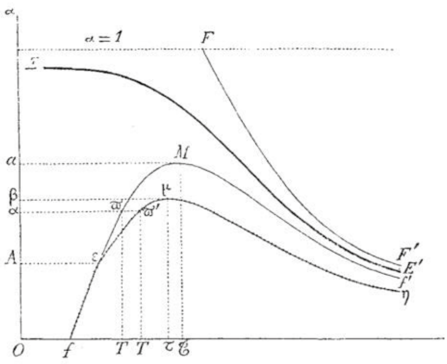

Figure 3 (Duhem P. 1896a, p. 160)

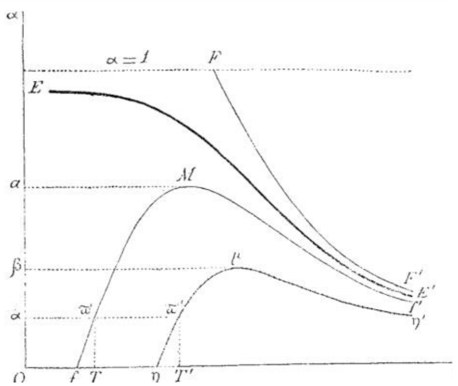

Figure 4 (Duhem P. 1896a, p. 163)

In the case of endothermic reactions, the region of dissociation split in the same way: the lower side, closer to the region of false equilibrium, was the seat of "mild" reactions, while the upper side, farther from equilibrium, was the seat of "explosive" reactions.[19]

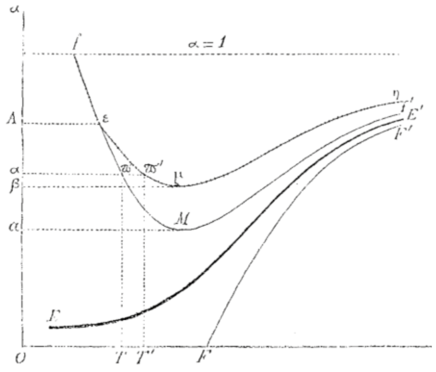

Figure 5 (Duhem P. 1896a, p. 162)

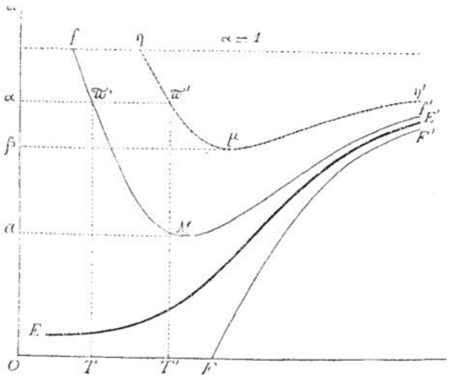

Figure 6 (Duhem P. 1896a, p. 166)

Duhem was aware that hypotheses and simplifications put forward in the course of the last chapters did not allow him to describe in a satisfactory way the complexity of phenomena. He was aware, in particular, that physical-chemical systems do not have "the same temperature in every point", nor the same pressure; moreover the living force does not undergo "negligible variations". In sudden and violent phenomena like explosions, those simplifications were probably un-

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[19] Duhem P. 1896a, p. 165.

suitable. In order to realise a better refinement, he imagined the system under consideration as a collection of small sub-systems to be analysed in accordance with the already known mathematical procedure.[20]

With the help of three new hypotheses, Duhem rephrased the study of combinations, in particular the propagation of "WAVES OF COMBINATION". Nevertheless, in the end, he found that even the new theoretical inquiry was based on "hypotheses which could not be realised": for instance, "diffusion" could not be disregarded in real chemical reactions, which were not purely adiabatic. Taming complexity was found to be too hard to pursue in a completely satisfactory way. The general equations of the theory had shown themselves to be potentially fruitful to describe a wide set of phenomena, but the theory seemed to creak under the weight of so many specific applications.

When, in the last chapter, Duhem undertook the conceptual path leading him back from chemical reaction to ordinary mechanics, he did not try to insist on specific applications. He discussed the structure of his general equations but, in the end, he invited the reader to make reference to a brief bibliography.[21]

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

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[20] See Duhem P. 1896a, p. 168: "Pour aborder avec plus de rigueur les phénomènes explosifs, il faut diviser le système étudié en éléments de volume, tenir compte des différences de pression sur les différentes faces de cet élément, des forces d'inertie, des actions de viscosité qui résultent de son mouvement, et appliquer seulement aux modifications qui se produisent à l'intérieur de chaque élément de volume des considérations analogues à celles qui précèdent."

[21] See Duhem P. 1896a, p. 178: "Nous ne développerons davantage l'étude du frottement de roulement, de glissement et de pivotement ; il nous suffit d'avoir montré comment cette étude se relie à la théorie générale que nous avons esquissée dans ce travail ; le lecteur soucieux de suivre les propriétés du frottement de deux corps en contact trouvera de précieux renseignements dans les écrits suivants : …."

term of *hysteresis*" from the other "terms already contained" in the equations was their behaviour with regard to time.

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

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

$$\ldots\ldots$$

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

contained only quadratic terms in $d\alpha/dt$,......,$d\lambda/dt$, and therefore they were invariant under the transformation $t \to -t$, even though $d\alpha/dt$,......,$d\lambda/dt$ 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 même 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*.[22]

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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[22] 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.[23]

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 ordi-

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[23] Duhem P. 1896a, p. 205.

> naire, irréalisables, hors de l'organisme, *dans les conditions de température où l'organisme fonctionne*.[24]

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 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?[25]

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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[24] 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.

[25] Duhem P. 1896a, p. 207.

AFTERWORD:
UNEARTHING A BURIED MEMORY

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"?[1]

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 "*transcendante à la méthode physique*". In order to decide the issue, scientists had to resort to the reasons of "Metaphysics", or to pragmatic

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[1] 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."

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 e 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".[2]

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 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

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[2] See Duhem P. 1903, in Duhem P. 1992, pp. 184, 186-9, and 190-93.

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".[3]

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".[4]

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.

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[3] 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 7.

[4] 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.

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.[5]

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 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*".[6]

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, de-

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[5] Duhem P. 1906, pp. 217, 274, 303, and 328.

[6] Duhem P. 1911, tome I, pp. 1-3.

velopment, 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.[7]

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.[8] 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 second level corresponds to wider-scope principles and hypotheses, and to their interplay. Finally, the third level corresponds

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[7] Duhem P. 1911, tome I, pp. 4-5.

[8] 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.

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 chapters of the present book, 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.[9]

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.

First of all, it is worth remarking that, in 1898, the mathematical physicist Helm had paid great attention to Duhem's theoretical physics. He opened his book on the history of *Energetics* with a very poetical passage which ended and sealed the paper that Duhem had devoted to the history of Optics in 1894.[10] Helm qualified Duhem as "the

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[9] 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.

[10] See Helm G. 1898, in Helm G. 2000, pp. 55 and 65. Helm had become Professor of Analytical geometry and Mechanics at Dresden University of Technology in 1888. At the end of the mentioned paper, Duhem had synthesised his historiographical view, where the superposition of two historical processes was at stake: the short-term turnover of specific physical hypotheses and models, and the long-term progress of physics. The last passage was extraordinary lyrical: this style was unusual for him. See Duhem P. 1894d, p. 125: "A l'heure où le flot monte à l'assaut d'une grève, une lame se forme, ondule, déferle et

ardent proponent of energetics in France", where Energetics was not intended as a specific theory but as "a *unified* development of thought" or "a comprehensive knowledge of nature" ("eine eigenartige Weise umfassender Naturerkenntnis"). It corresponded to a representation of natural processes "as *immediately as possible, without* the aid of invented mechanical devices". It aimed at "a great reorientation in the human understanding of natural events".

In the seventh part of the book, Helm mentioned Duhem's mathematical generalisation of "differential work" and "differential heat", which went far beyond the representation of energy as a sum of products between "*intensities*" and "*capacities*" or "*quantity functions*". Helm's attitude towards Mechanics was not so different from Duhem's: he aimed to "make mechanics useful for non-mechanical processes, but without a mechanical hypothesis". For the implementation of that meta-theoretical design he could rely on the principle of conservation of energy ("das Perpetuum-mobile-Prinzip"), and on a "principle of analogy", The latter was nothing else but the structural analogy between the equations of Analytical Mechanics and the equations describing non-mechanical processes, which Helm attributed to Helmholtz and J.J. Thomson.[11]

In the eighth part of his book, Helm discussed in some detail "Duhem's work", which was based "entirely on the foundations of thermodynamics". At the same time, Duhem's "generalised thermodynamics" relied on "mechanical analogies", in order to go "beyond the limits of classical thermodynamics". He mentioned Duhem's "investigations" into "*friction*, *viscosity*, elastic *aftereffects* and *hysteresis*", and stressed the difference between the tradition of "mechanics" and "mechanical conception". According to Helm, Duhem had shown that it was "altogether unnecessary to sacrifice the ideas with which we are familiar from mechanics" just for "the sake of energetics". The

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couvre le sol sec jusque-là ; mais, aussitôt, il lui faut abandonner sa conquête, laisser assécher le sable qu'elle avait couvert, et se perdre dans la lame qui se forme derrière elle ; ce fracas des lames, qui ne surgissent que pour s'écrouler, semble un vain effort de la mer, donnant un peu d'écume et un peu de bruit ; cependant, deux heures plus tard, la grève où vous avez marqué vos pas dort sous la profondeur des eaux ; par l'incessant va-et-vient des lames qui se dressent et qui se prisent, qui avancent et qui reculent, sans relâche, l'Océan a monté."

[11] Helm G. 1898, in Helm G. 2000, pp. 314, 363, and 375-6.

mechanical conception attempted "to subjugate new experiences to the old ideas"; on the contrary, "Duhem's energetic method" revived and revised "old ideas by means of the new experiences".[12]

In 1917, one year after Duhem's death, Émile Jouguet, *Ingénieur en chef des Mines*, and *Répétiteur à l'École Polytechnique*, published a paper in the *Revue générale des Sciences pures et appliquées*, where he gave a short account, and attempted a comprehensive appraisal of Duhem's contribution to theoretical physics. Jouguet had followed the tradition of French engineers who, in the second half of the nineteenth century, had steered French physics out of the arid lands of mere experimentalism. He appreciated both Duhem's physics and Duhem's meta-theoretical commitments. He reminded the readers that "Duhem had a very peculiar place in French science": he had not taken part in the building up of "recent theories", and "his method contradicted some habits". His theories could be understood at the price of "efforts which some people were not able to make". Jouguet emphasised both "the originality of his mind" and "the flaws in most of his writings", being the latter due to "the breadth of his interests", and "the fast pace of his work". In the end, however, an attentive reader could not be but struck by the "wealth and originality" of Duhem's scientific practice, which he qualified as "very deep, mindful, and personal".[13]

Jouguet was aware that Duhem's pathway to Thermodynamics had stemmed from the researches of Massieu, Gibbs and Helmholtz. The structural analogies Duhem had put forward between "mechanical Statics" and "thermodynamic Statics" had led him far from the hypothesis of heat "as a kind of motion" or "molecular frantic drift". His generalised mechanics had nothing to do with specific mechanical or kinetic models: it was rather a structural or abstract model of explanation. Duhem's generalised mechanics was a science of motion in a general sense, or a science of transformations, according to the mean-

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[12] Helm G. 1898, in Helm G. 2000, pp. 383-7.

[13] Jouguet E. 1917, p. 40. In 1908-9, Jouguet had published a two-volume history of Mechanics, *Lectures de Mécanique*, whose first claim was the usefulness of history in order to "better understand the nature of principles and laws of Mechanics". In the *Préface*, he acknowledged the role played by Duhem in the comprehension of the ancient sources of modern mechanics. Moreover, when he briefly discussed peripatetic physics, he stressed the deep theoretical connections among that ancient physics, dissipative processes, and "the foundations of Thermodynamics". See Jouguet E. 1908, pp. VII-VIII and 4.

ing of the word "motion" in peripatetic tradition. As Jouguet reported, "Mechanics and Thermodynamics were particular implementations of a single theoretical approach": a unified science could describe "changes of state as well as changes of place".[14]

Jouguet considered Duhem the founding father of "thermodynamics of irreversible processes": before his mathematical theories on "viscosity, friction, and hysteresis", those phenomena had been taken into account only "exceptionally". Moreover, new "differential equations of motion" in a general sense stemmed from Duhem's "chemical Mechanics", namely differential equations of the first order, corresponding to "variables without inertia". Those equations, just like the equations of ordinary mechanics, were "specific instances of the equations of Energetics". In this sense, *Energetics* encompassed different kinds of Mechanics, corresponding mathematically to different kinds of differential equations.[15]

Jouguet's meta-theoretical remarks deal with the debated concept of "Mechanism". He qualified Duhem as a "mechanic", but then he specified that "a mechanic should not be identified with mechanical attitudes". The statement could sound misleading unless we distinguish accurately between the two traditions which emerged in the history of Mechanics: on the one hand, the specific mechanical models, on the other, Analytical Mechanics. Duhem's mechanical approach was a *structural* Mechanism stemming from the latter tradition.[16]

In 1922, at the annual session of the *Académie des sciences*, the mathematician and mathematical physicist Émile Picard reported on "the life and work" of Duhem. He remarked that Duhem was more

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[14] Jouguet E. 1917, p. 41. The Jouguet word I have translated into "theoretical approach" is "doctrine".

[15] Jouguet E. 1917, pp. 43-5.

[16] Jouguet E. 1917, pp. 48-50. It is worth quoting some passages of Jouguet's appraisal: "C'est dans l'Energétique qu'il a trouvé l'outil permettant de construire, d'après cette méthode, une Mécanique applicable non seulement aux déplacements, mais encore aux transformations physiques et chimiques. L'Enérgétique supplée à l'insuffisance que manifeste la Mécanique classique dès qu'elle s'attache à des mouvements accompagnés de changements d'états. Mais, circonstance bien remarquable, elle use des procédés tout à fait analogues à ceux de cette dernière doctrine : sa Statique est un épanouissement du principe des vitesses virtuelles, sa Dynamique une extension du principe de D'Alembert et des équations de Lagrange." (*Ibidem*, p. 50)

appreciated by mathematicians than by physicists and chemists, although he “wanted to be a theoretician of Mechanics, Physics, and Chemistry”. He had been looked upon as “too physicist by the mathematicians, but also too mathematician by physicists and chemists”. The book he had published in 1886 on the chemical applications of thermodynamic potentials had attracted the mathematicians, because of the analogies with “Rational Mechanics, to which the mathematicians were accustomed”. Duhem had managed to catch the deep conceptual links between some “physical insights” stemming from “ancient ages”, and “certain views of contemporary science”. He had dared to dig “below the superficial layer” of philosophic tradition, where ancient theories had been preserved as “dead and fossilised” heritage.[17]

In 1927, the physicist Octave Manville, “chargé de conférence” at the faculty of Science at Bordeaux university, published an extensive book on Pierre Duhem’s physics. Two “Mémoire” concluded the book: in the first, the mathematician Jacques Hadamard commented on Duhem as a mathematician; in the second, the historian André Darbon commented on Duhem as a historian. Manville’s analysis is quite detailed, and for many decades his book remained the sole study on Duhem’s theoretical physics. He pointed out that Duhem’s choice of mathematising “qualities” stemmed from the rejection of every distinction between quantities and qualities, namely every distinction between primary and secondary features of a body or process. In its turn, this rejection stemmed from the distrust in every pretension of explaining the natural world. No hidden structures could lead us to catch “the real features of bodies”; nothing interesting could lie underneath their “tangible aspect”.[18]

In part, Manville blurred the context of Duhem’s third pathway to Thermodynamics. To the first pathway, which corresponded to the representation of heat as “a kind of motion of tiny corpuscles”, he associated the names of Gibbs and Helmholtz. To the second, which looked upon Thermodynamics as “independent of whatever hypothesis on the nature of heat”, he associated the name of Clausius,

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[17] See Picard É. 1922, pp. CI, CIII-CIV, CVI, and CXXXV.

[18] Manville O. 1927, pp. 18-9.

who had also theorised on the kinetic theory. He placed Duhem on the same pathway as Rankine, who had looked upon Rational Mechanics as "a specific instance of a general Thermodynamics". Manville claimed that the kinetic theory "could not account for *irreversible* phenomena". Maxwell and Boltzmann had assumed that our "*macroscopic* observations" involved "a huge number of molecules". Macroscopic physical quantities corresponded to a sort of "*average state*", and the "Carnot-Clausius principle" could not be completely satisfied on a "molecular scale". In that context, it was "natural" that a gas "evolved" towards "states corresponding to a higher number of complexions". Boltzmann had identified those states with "the most probable" ones, but Manville considered questionable that "definition" of probability.[19]

According to Manville, Duhem had managed to conflate "classic Dynamics" and the "Theory of conduction of heat"; at the same time, he had managed to explain why the two fields of physics "had evolved in an independent way". Duhem's scientific enterprise could be synthesised into two stages. In the first stage, he had accomplished the unification between the mechanical theory of heat, where heat is transformed into work without any conduction, and the theory of heat conduction, where thermal conduction does not perform any mechanical work. In the second stage, he had realised the unification between Rational Mechanics and the already unified theory of heat. In brief, he had managed to unify the traditions associated to Lagrange, Carnot and Fourier. Duhem's physics appeared to Manville as "a chain whose ends" corresponded to "systems wherein *inertial actions* dominated", and systems wherein those actions could be neglected. In fact, among the new concepts that had emerged from Duhem's theoretical physics, Manville mentioned the "*variables without inertia*", namely variables whose variations did not entail that the body "moves *locally*".[20]

Step by step, a hierarchy of increasing complexity had emerged: starting from "the simplest phenomena", Duhem had faced "the physics of *viscous media*", then the physics for "systems with *friction*", and finally "systems with hysteresis". New concepts had emerged:

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[19] Manville O. 1927, pp. 27 and 45-6, footnote 2 included.

[20] Manville O. 1927, pp. 66, 69, 75, and 90.

the "*false equilibrium*", where "an *infinite number of states of equilibrium* which classic Thermodynamics could not account for" really existed, and the distinction between "*seeming viscosity*" and viscosity which "had to appear essentially and necessarily in the equations".[21]

In the first decades of the twentieth century, some kind of unification between physics and chemistry through a generalisation and re-interpretation of Analytical Mechanics really took place. The physicist and historian of physics René Dugas pointed out the formal link between Quantum Physics and the tradition of Analytical Mechanics. What we usually call Quantum Physics aimed to describe atomic structure and chemical bonds through a re-interpretation of Lagrangian and Hamiltonian formalism, at least in extremely simple configurations. Dugas found a meaningful structural analogy between Duhem's widening of the Lagrangian approach, and the quantum re-interpretation of Hamilton's formalism. He saw them as very different implementations of a similar second-level design.[22]

Dugas was able to re-interpret Duhem's anti-atomism in a non-trivial way. He specified that Duhem did not rely on atoms as real *things*: in his view, atoms could only be considered as mere representations. From the methodological point of view, they were not so different from the mathematical models of continuous media, which Du-

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[21] Manville O. 1927, pp. 91, 93, and 97. Different kinds of irreversibility existed in physics, because different "abnormal branches stem from the main trunk of *Energetics*". If one branch was represented by "the theory of *friction* and *false equilibrium*", another corresponded to "*permanent deformations* and *hysteresis*". Manville acknowledged that Duhem had not managed to put forward a satisfactory theory for permanent deformations, even though he had tried to outline very sophisticated theories dealing with hysteresis in "*fast transformations*", and "*the simultaneous existence of hysteresis and viscosity*". See Manville O. 1927, pp. 135-6, 154, 175, and 429.

[22] We can even assume an a-priori *incommensurability* between Duhem's 1896 theoretical sketch and late-1920s Quantum Physics: indeed, with regard to the first-level specific theoretical models, any kind of comparison would be meaningless. See Dugas R. 1937, p. 70: "Dans l'arsenal des théorèmes de Lagrange, Hamilton, Jacobi, la physique quantique a trouvé la base de départ dont elle avait besoin ; l'équation de Jacobi, sous forme classique ou relativiste, domine la théorie des modèles de Bohr ; l'équation de Schrödinger prolonge celle de Jacobi. Une nouvelle preuve est apportée par la formulation de la mécanique quantique à l'aide d'une extension des crochets de Poisson : une notation sans valeur intrinsèque de la mécanique analytique classique devenant, grâce à un postulat restrictif sur la commutativité de la multiplication, un outil essentiel permettant d'écrire les équations du mouvement sans la connaissance préalable de variables canoniques."

hem relied on. Dugas found that this kind of abstract representation and methodological attitude was just revived by Quantum Physics.[23]

In 1941, the American experimental physicist Percy William Bridgman published a book on the foundations of Thermodynamics, *The nature of Thermodynamics*. The original edition was reproduced in 1961 "with no essential change" according to Bridgman himself. Although Bridgman's approach to Thermodynamics was not so different from Duhem's, he never mentioned him, and it is debatable whether he had previously run up against Duhem researches. The fact is that in the 1940s the Duhem scientific legacy had already become a sort of buried memory. In those years, the scientific community was concentrating its intellectual and material resources on sub-nuclear physics. The interest in the foundation of Thermodynamics, and the foundation of physics in general had progressively faded away. The new theoretical physics was quite different from the wide-scope theoretical physics of the late nineteenth century.[24]

Bridgman remarked that "most of the systems of practical interest are completely surrounded by irreversibility", that "the entropy of such systems is not defined in the classical universe of discourse", that "all living systems are of this nature and technically the concept of entropy may not be applied to such systems", and that "a generalized entropy may be defined". The existence of phenomena like hysteresis was "embarrassing", because the notions of "state" and "property", as they were "commonly used", involved only "operations which can be performed on the body *now*", and did not involve "a knowledge of past history". In general, there were "objects" which

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[23] Moreover, from the methodological point of view, the complex relationship between results of experiments and theoretical entities like quantum operator weakened even the concept of *experimentum crucis*, which had been criticised by Duhem. See Dugas R. 1937, p. 69: "Rappelons à ce sujet que réfutait l'existence de tout *experimentum crucis*, ceci en vertu de la transcription symbolique que subit dans la théorie tout fait d'expérience. […] C'est ainsi qu'en optique aucune expérience, contrairement à l'affirmation d'Arago, ne permet de décider de la nature corpusculaire ou ondulatoire de la lumière. Il en va de même pour la matière, depuis l'introduction des quanta. […] Les *opérateurs* que l'on rencontre en mécanique quantique ne sont pas tous doués de sens physique ; les observables elles-mêmes ne sont que des objets du second ordre, analogues rationnels d'objets du sens commun."

[24] Bridgman mentioned "de Groot, Prigogine, and especially Onsager". See Bridgman P.W. 1961, p. v.

could not be “handled by the conventional thermodynamics”: among them he mentioned “the capricious freezing of a sub-cooled liquid”, and “atomic disintegration”.[25]

He regretted that “the two laws to which the physicists ascribe the most sweeping universality“ were “simply” labelled “first and second laws of *thermodynamics*”. He also questioned the explanatory power of the kinetic theory. In some way, kinetic theory was a microscopic extrapolation of macroscopic mechanics: it sounded quite strange that such an extrapolation could explain macroscopic thermodynamics, or could possess any explanatory power. According to Bridgman, “the essential fact that logically the microscopic picture had its origin in the macroscopic” could not be overlooked. Even the physical and mathematical link between entropy and “disorder” was questionable: he found that “this coupling is not always felicitous”: “disorder” could not be looked upon as “a thermodynamic concept at all”.[26]

He also found debatable that we could “assign a meaning simultaneously to flux of mechanical energy and flow of heat”. He remarked that, “in the case of small-scale turbulent motion in a liquid”, the two fluxes could not be clearly separated: the difficulty appeared to be “particularly formidable in the case of radiant energy”. Some kind of unification between Mechanics and Thermodynamics was required. The fact is that, when we scan the phenomena occurring at every scale of length, from the microscopic to the macroscopic level, we cannot find a definite threshold separating micro from macro, or heat flux from the flux of mechanical energy. Bridgman also dared to imagine that phenomena we now qualify as “mechanical” could be “special kinds of plateau phenomena”, which would become “thermal” when considered “from the point of view of a time scale extravagantly longer than that available to us”. Even in the simple case of friction,

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[25] Bridgman P.W. 1961, pp. vi, 62, and 64.

[26] Bridgman P.W. 1961, pp. 8-9, 106-7, and 174-5. Bridgman briefly discussed a simple case: “Consider, for example, a quantity of sub-cooled liquid, which presently solidifies irreversibly, with increase of entropy and temperature, into a crystal with perhaps a regular external crystal form and certainly a regular internal arrangement as disclosed by X-rays. Statistically, of course, the extra ‘disorder’ associated with the higher temperature of the crystal more than compensates for the effect of the regularity of the crystal lattice. But I think, nevertheless, we do not feel altogether comfortable at being forced to say that the crystal is the seat of greater disorder than the parent liquid.” (*Ibidem*, pp. 174-5)

"the external universe delivers mechanical work which the system receives as heat".[27]

We cannot leave Bridgman's book before mentioning a metatheoretical remark which Duhem had expressed in almost the same words: the aim of a physical theory, thermodynamics in particular, was not the "explanation" of "macroscopic phenomena" in terms of microscopic motions. Thermodynamics was not required to explain "the origin of the equation of state of a gas, but treats it as given". Nor "an excursion into the atomic domain" was required; moreover that excursion involved the extrapolation from macroscopic to microscopic systems, which was just the kind of logical short-circuit that Bridgman had already pointed out.[28]

Duhem's attempt to tame complexity received a meaningful implementation in 1947, in Prigogine's essay *Etude Thermodynamique des Phénomènes irréversibles*. He pointed out "*the deficiencies of classic thermodynamics*", and listed some of them. First of all, classic thermodynamics was "confined to states of equilibrium and reversible transformations", and could not account for chemical reactions, wherein the system is not in chemical equilibrium. Secondly, the two principles of classic Thermodynamics were confined to closed systems, namely systems allowed to exchange energy but not matter with the external world. Other difficulties arose from the applications to electro-chemistry or to systems crossed by a thermal gradient. According to Prigogine, a more general Thermodynamics was required, in order to account for irreversible phenomena, states far from equilibrium, and open systems.[29]

Prigogine acknowledged explicitly the role played by Duhem in the setting up of a new Thermodynamics, even though his researches had not been received as they deserved. The importance Duhem had given to Clausius' "uncompensated heat" appeared to Prigogine the starting point for a more general thermodynamics. Prigogine defined the entropy of a system as the sum of two contributions,

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[27] Bridgman P.W. 1961, pp. 55, 67, 69, 72, 153, 192-3, and 231.

[28] Bridgman P.W. 1961, pp. 222-3.

[29] Prigogine I. 1947, pp. 3-5.

$$dS = \frac{dQ}{T} + \frac{dQ'}{T},$$

where dQ was the heat received from outside in the time dt, and dQ' was just Clausius' uncompensated heat. The latter emerged from irreversible processes taking place inside the system: it was therefore intrinsically positive. Even in the case of adiabatic transformations, when the system could exchange neither matter nor energy with the outside, we had $dS > 0$. There were both a "*transfer*" and a "*production*" of entropy: $dS = d_e S + d_i S$. In its turn, the *transfer* of entropy in open systems was due to two different processes: transfer of heat and transfer of matter. Prigogine reminded the reader that all complex systems, namely the systems belonging to our real world, are open systems. We find open systems "in meteorology and in many technical applications", and in biology, where "they play a fundamental role". To sum up, entropy production was linked to both "transport phenomena (thermal conductivity, viscosity, and diffusion) and chemical reactions".[30]

Prigogine found a sort of complementarity between Duhem's third pathway to Thermodynamics and Maxwell-Boltzmann's first way: the two "methods" could merge with each other "harmonically". Macroscopic thermodynamics offered "the functional relations", and the kinetic theory offered "the numeric values of coefficients to be found in these relations, when the kinetic theory is applicable". The "thermodynamics of irreversible phenomena" represented a necessary counterpart to mechanics and electromagnetism in the field of "macroscopic physical theories". At the same time, it offered a unifying framework just for that wide field.[31]

In the context of thermodynamics of irreversible processes, time could be looked upon as more than a mere "scalar" entity: according to Prigogine, whenever "the flow of time plays an essential role", Thermodynamics was at stake. When we state that "there is always

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[30] Prigogine I. 1947, pp. 1-3 and 95-9. See also p. 20 for the relationship between entropy and Gibb's molar potential.

[31] Prigogine I. 1947, pp. 9-10 and 76-81. With regard to the structural link between Mechanics and Thermodynamics, it is worth mentioning that, when Prigogine outlined a general thermodynamics for "non-uniform systems", he started from the analogy with the mechanics of continuous media.

production and never destruction of entropy", we also state an asymmetry between past and future: thermodynamics leads us to assume "the existence of a preferred direction past-future in the flow of time". In the last chapter of the essay, Prigogine deepened the mathematical side of the relationship between thermodynamics and time. Starting from Eddington's remark on the relationship between time flow and dS/dt, Prigogine tried to define "a new scale of time" linked to "the production of entropy". The thermodynamics of irreversible phenomena would have allowed physicists to compute "the duration of a phenomenon by means of its *content of irreversibility*".[32]

He put forward different mathematical laws connecting astronomical time to thermodynamic time, and the corresponding functions were non-linear. Although the chain of assumptions and approximations in his deduction is questionable, Prigogine managed to show that a new different definition of time could be put forward, and it led to a concept of time closer to the events of the physical world. In some way, even the astronomical time is drawn by the physical world: it deals with the quasi-regular motion of sun and planets. Nevertheless, thermodynamic time would have a wider scope, because it spans physics, chemistry, and perhaps the sciences of life. He even imagined a plurality of *times*, and the possibility of choosing the most suitable *time* for a specific kind of phenomena.

Some kinds of thermodynamic *times* could be more suitable for living beings: indeed, metabolic processes were "the seats of irreversible phenomena". Prigogine's time was a complex entity, far from the abstract purified concept which had emerged together with modern science. It was a "*local*" time, for it was "generated by irreversible processes taking place in a well-defined space". At the same time, thermodynamic time could aspire to a greater generality in the context of the recent physical theories. Differently from astronomical time, which was only the component of a four-vector, thermodynamic time stemmed from a relativistic invariant, namely entropy.[33]

After some years, Prigogine published a book in English, which was intended as a first systematization of the same subject matter: the

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[32] Prigogine I. 1947, pp. 11, 133 and 135-6. Prigogine showed the possibility of defining consistently two kinds of time: the well-known astronomical time t, and the time τ stemming from the production of entropy $\sigma[S]$.

[33] Prigogine I. 1947, pp. 136-8.

thermodynamics of irreversible processes. At that time, the theory had already led to “a large number of applications”. In the “Preface”, Prigogine reminded the reader that “classic thermodynamics” confined itself only to “reversible processes” and “true equilibrium states”. In reality “the majority of phenomena” in the fields of astrophysics, meteorology, geology, and biology dealt with “irreversible processes which take place outside the equilibrium state”. From the mathematical point of view, reversible processes were expressed by equations like “the wave equation which describes the propagation of waves in a non-absorbing medium”:

$$\frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}=\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}.$$

Irreversible processes were mathematically expressed, for instance, by the “Fourier equation for temperature”:

$$\frac{1}{\alpha}\frac{\partial T}{\partial t}=\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}.$$

If the former was invariant under the transformation $t \to -t$, the latter was not. The second equation broke the symmetry between past and future, which was a fundamental feature of mechanics.[34]

Irreversible transformations and processes far from equilibrium took place in open systems, where the environment came into play. If *isolated* systems could exchange neither matter nor energy with the environment, and *closed* systems could exchange only energy, *open* systems could “exchange both energy and matter with the exterior”. According to Prigogine, open systems were the most suitable kind of systems for representing complexity in both physics and biology. In open systems, it is useful to split the variation of “extensive”, namely additive, variables into two components of different nature: an external component, “due to exchanges with the exterior”, and an internal component “resulting from reactions inside the system”.[35]

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[34] Prigogine I. 1955, pp. V-VI, and 14.

[35] Prigogine I. 1955, pp. 3-7. This split had already been put forward by Prigogine in 1947, and applied to entropy, mass and energy. See Prigogine I. 1947, pp. 1-3 and 95-9.

In particular, Prigogine stressed the importance of "stationary non-equilibrium states". The adjective "non-equilibrium" means that the production of entropy is different from zero; the adjective "stationary" means that the behaviour of the system does not depend on time. In this case,

$$\frac{dS}{dt}=\frac{d_eS}{dt}+\frac{d_iS}{dt}=0.$$

As $d_iS/dt>0$, we "necessarily have" $d_eS/dt<0$. This means that "stationary non-equilibrium states cannot occur in isolated systems": a flow of entropy "is necessary to maintain the stationary state". We could say that the system can preserve its stationary condition only by sending out entropy towards the environment, therefore increasing the entropy of the environment. Prigogine emphasised the importance of phenomena of this kind in "biological processes".[36]

After the second World War, the buried memory of Duhem's theoretical physics re-emerged here and there, in one way or another. In 1950, in France, Dugas acknowledged the role played by Duhem and Jouguet in his own scientific training and intellectual education. Duhem had developed the tradition of "Lagrange *analytical* mechanics" as opposed to "Poisson *physical* mechanics". Besides "a general mechanics based on Thermodynamics" Dugas saw in Duhem "a reaction against Cartesian and atomistic conceptions", and a return to "the deepest principles of peripatetic doctrine".[37] In 1956, in the United States, the chemical-physicist Donald G. Miller put forward an approach to the thermodynamics of irreversible processes which was not so different from Duhem's *Energetics*, apart from some naïve remarks on the alleged simple derivation of "axioms" from experiments. He reminded the reader that "[T]he only processes which can

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[36] Prigogine I. 1955, pp. 74, 82, and 89. Prigogine believed that the thermodynamics of irreversible processes in open systems could allow scientists to better understand life See p. 91: "The behaviour of living organisms has always seemed so strange from the point of view of classical thermodynamics that the applicability of thermodynamics to such systems has often been questioned. One may say that from the point of view of the thermodynamics of open and stationary systems a much better understanding of their principal features is obtained."

[37] Dugas R. 1950, pp. 442-3.

be treated in detail" by classic thermodynamics "are the physically unrealizable reversible ones". As Prigogine had done some years before, Miller also stressed the difference between "the entropy produced *inside the system*" ΔS_i, and "the entropy *added to the system* by heat transport across its boundaries": the former stemmed from "the more familiar uncompensated heat of Clausius".[38]

In 1977, in his *Nobel lecture,* Prigogine emphasised the deep link between the concept of time and the second Principle of Thermodynamics. At the same time, he stressed the role recently played by Thermodynamics in the "reformulation of (classical or quantum) mechanics". In its connection with "irreversibility" and "history", time had become something more than a mere "geometrical parameter associated with motion". In complex systems, like "a town", or "living systems", or "biochemical cycles involving oscillatory enzymes", far from thermodynamic equilibrium, "dissipative structures" could emerge over time: in some way, "non-equilibrium" could become "a *source of order*".[39]

A striking instance was offered by "Bénard instability", where ordered convective streams emerged in a liquid layer submitted to a "sufficiently large" gradient of temperature. Although "entropy production" increased, the layer was in a higher "state of organization" than the state of rest. Contrary to what we should expect on the grounds of Boltzmann thermodynamics, the "almost zero probability" state of order in Bénard convection corresponded to a high value of entropy. These "dissipative structures" could only emerge in open systems, namely physical systems able to exchange both matter and energy with their environment. The order was due to "a giant fluctuation stabilized by exchanges of energy with the outside world".[40]

Prigogine stressed that far from equilibrium the behaviour of a physical system "may become very specific", whereas "[t]he laws of

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[38] The second volume of Duhem's 1911 treatise is only mentioned in a footnote in connection with the computation of entropy production in specific cases: viscosity and heat conduction. In another footnote, Duhem is mentioned because he had mentioned Stokes and some symmetries in linear relations between forces and fluxes. Duhem does not appear in the list of "important monographs" which, in Miller's words, "[t]his survey is primarily based on". See Miller D.G. 1956, p. 433, fn. 1, p 434, and p. 436, footnote 11 included.

[39] Prigogine I. 1977, pp. 263-4. In 1977 Prigogine won the Nobel Prize for Chemistry.

[40] Prigogine I. 1977, p. 267.

equilibrium are universal". The state of the system could experience bifurcations: little changes in the initial state could give place to ample fluctuations which led the system to sudden transition towards stable or instable "branches". Those bifurcations stemmed from the non-linearity of the differential equations describing the transformations. In "autocatalytic reactions" like "the so-called Brusselator", the chain of chemical reaction could be described by the non-linear differential equations.[41]

When we increase the value of a parameter λ, for instance the concentration of a certain chemical compound "in the Brusselator scheme", multiple solutions of the system of differential equations really appear. According to Prigogine, in some way bifurcations introduced two crucial features into physics: "history" and indeterminism. If we assume that the physical system "is in the state C and came there through an increase of the value of λ", then the "interpretation" of this state entails the knowledge of "the prior history of the system", namely the passage through A and B. The system follows "deterministic laws" in every branch "between two bifurcation points", whereas "fluctuations" decide what branch it will follow "in the neighbourhood of the bifurcation points".[42]

Meanwhile, the design of a generalized and fully mathematized Thermodynamics had been put forward by Clifford A. Truesdell in the 1960s. In the second edition (1984) of his book *Rational Thermodynamics*, he reminded the reader that he had "returned to the sources" of Thermodynamics. In the second half of the nineteenth century some scholars had attempted to bridge the gulf between the two traditions that had emerged in the first half: "the FOURIER *line*, which considered *workless dissipation*", and "CARNOT *line*, which considered *dissipationless work*". He remarked that, in the last decades of the nineteenth century, "thermodynamics was already regarded in Germany as a dead field, insusceptible of broadening or deepening". The majority of physicists had confined themselves to equilibrium states: as a

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[41] Prigogine I. 1977, pp. 270-1. "Brusselator" was the name given to a specific kind of autocatalytic reaction or "*chemical watch*". See Prigogine I. and Nicolis G. 1977, pp. 93-4, and Progine I. and Stengers I. 1986, pp. 223-8.

[42] Prigogine I. 1977, p. 273.

consequence, Thermodynamics was "inapplicable to *natural processes*", namely real, irreversible phenomena.[43]

According to Truesdell, Duhem represented an outstanding exception. Even though he appreciated Bridgman's efforts to cope with the foundation of Thermodynamics in the 1940s, he found that Bridgman had "failed to reach the clarity, the definiteness, or the conceptual level maintained fifty years earlier by DUHEM". Truesdell regretted that "DUHEM's work had fallen into the general oblivion of classical mechanics in the interbellum", although "most of the work since 1960" had followed "the example of DUHEM". He recommended that "DUHEM's researches be studied until justice be done them", and qualified Duhem's Preface to his *Treatise on Energetics or General Thermodynamics* as a "program of modern rational thermodynamics".[44]

Truesdell remarked that, before Duhem, Thermodynamics had fluctuated between technology and cosmology: he saw the interpretation of thermal engines, on the one hand, and "the speculations about the universe", on the other. Thermodynamics had "always had a hard time striking a mean between these extremes": while "its claims" had often been "grandiose", its applications are usually trivial". Furthermore, the mathematics of thermodynamics appeared to Truesdell obscure and misleading. He aimed to state and teach Thermodynamics "just as classical mechanics is stated precisely and learned". Truesdell's aim was not different from Duhem's: in Truesdell's words, he was himself looking for "a thermodynamic theory formally similar to the classical one but vastly more general in scope". Generalized Thermodynamics should "extend the concepts of mechanics so as to allow for diffusion and chemical reactions as well".[45]

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[43] Truesdell C. 1984, pp. 2, 7, 24-5. It is worth mentioning that, in 1964, Louis de Broglie stressed a fundamental formal analogy between Analytical Mechanics and Thermodynamics. From the relativistic point of view, Hamiltonian "action" is the "fundamental invariant of Mechanics", and entropy is "the fundamental invariant of Thermodynamics". De Broglie remarked that the relativistic invariance was consistent with Boltzmann's interpretation of entropy as "an integer number of complexions". See De Broglie L. 1964, pp. 25 and 49.

[44] Truesdell C. 1984, p. 38, 40-1 and 45.

[45] Truesdell C. 1984, pp. 59, 61-2, and 106. With regard to mathematics, he regretted that the readers of textbooks on Thermodynamics had to face equations like $T \cdot dS \geq \delta Q$. See p. 61: "He is told that dS is a differential, but not of what variables S is a function; that δQ is a small quantity not generally a differential; he is expected to believe not only that a dif-

What Truesdell called "modern continuum thermodynamics" consisted of a "collection" of theories concerning "elastic materials", "viscous materials", "materials with memory", "mixtures", and so on. Nevertheless, all these branches of physics were based on the same principle: the "Clausius-Duhem inequality". In brief, *"for any process suffered by any body composed of the material under study"*, Rational Thermodynamics assumed

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

" dq denoting the element of heat received from external sources and ϑ the temperature of the part of the system receiving it". Truesdell claimed that this inequality could be applied to "general motions", far beyond the states of equilibrium: to deny this was to deny "that there can be such a thing as a thermodynamics of irreversible processes".[46]

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.[47]

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ferential can be bigger than another, but even that a differential can be bigger than something which is not a differential."

[46] Truesdell C. 1984, pp. 123 and 157. The *Clausius-Duhem* inequality was explicitly mentioned by Truesdell for the first time in 1960, in the long essay "The Classical Field Theories" he published in 1960 together with Richard Toupin. (I thank Sandro Caparrini for this information.) In the second half of the twentieth century, other mathematical physicists developed what we call rational thermodynamics: among them, Bernard Coleman and Walter Noll.

[47] 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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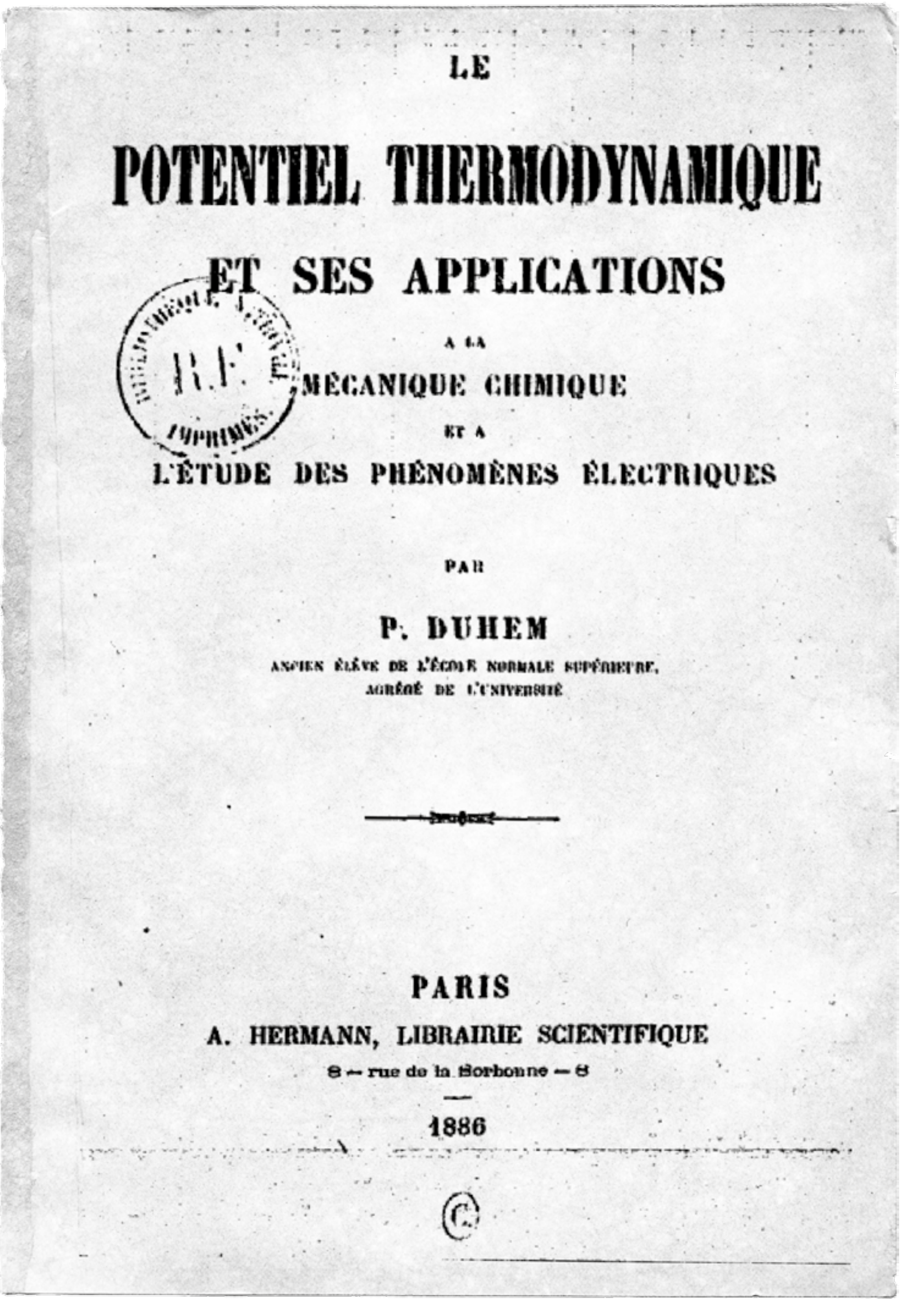

LE

POTENTIEL THERMODYNAMIQUE

ET SES APPLICATIONS

A LA

MÉCANIQUE CHIMIQUE

ET A

L'ÉTUDE DES PHÉNOMÈNES ÉLECTRIQUES

PAR

P. DUHEM

ANCIEN ÉLÈVE DE L'ÉCOLE NORMALE SUPÉRIEURE,
AGRÉGÉ DE L'UNIVERSITÉ

PARIS
A. HERMANN, LIBRAIRIE SCIENTIFIQUE
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642.

THÈSES

PRÉSENTÉES

A LA FACULTÉ DES SCIENCES DE PARIS

POUR OBTENIR

LE GRADE DE DOCTEUR ÈS SCIENCES MATHÉMATIQUES,

Par M. P. DUHEM,

Maître de Conférences à la Faculté des Sciences de Lille.

1re THÈSE. — De l'aimantation par influence.
2e THÈSE. — Propositions données par la Faculté.

Soutenues le 30 ~~nove~~Oct mbre 1888, devant la Commission d'Examen.

MM. DARBOUX, *Président*.
POINCARÉ, } *Examinateurs*.
BOUTY, }

PARIS,
GAUTHIER-VILLARS ET FILS, IMPRIMEURS-LIBRAIRES
DU BUREAU DES LONGITUDES, DE L'ÉCOLE POLYTECHNIQUE,
Quai des Grands-Augustins, 55.

1888

INTRODUCTION

A LA

MÉCANIQUE CHIMIQUE

PAR

P. DUHEM

CHARGÉ D'UN COURS COMPLÉMENTAIRE DE PHYSIQUE MATHÉMATIQUE
ET DE CRISTALLOGRAPHIE A LA FACULTÉ DES SCIENCES DE LILLE

PARIS
GEORGES CARRÉ, ÉDITEUR
58, Rue St André-des-Arts

1893

THÉORIE THERMODYNAMIQUE

DE LA VISCOSITÉ, DU FROTTEMENT

ET

DES FAUX ÉQUILIBRES CHIMIQUES

Par P. **DUHEM**

PROFESSEUR DE PHYSIQUE THÉORIQUE A LA FACULTÉ DES SCIENCES
DE BORDEAUX

Extrait des *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux*,
t. II (5e Série).

PARIS
LIBRAIRIE SCIENTIFIQUE A. HERMANN,
LIBRAIRE DE S. M. LE ROI DE SUÈDE ET DE NORVÉGE,
8 – rue de la Sorbonne – 8

1896