

UNIVERSITÀ DEGLI STUDI DI BERGAMO

Facoltà di Scienze della Formazione

Dottorato in Antropologia ed Epistemologia della complessità

XXIII ciclo 2008-2010

TAMING COMPLEXITY

Duhem pathway to Thermodynamics

Supervisore: Chiar.mo Prof. Enrico Giannetto

Tesi di Dottorato

Stefano BORDONI

Matricola n. 1004436

“Read with proper care,
he usually turns out
to have seen farther than his critics”
(Martin R.N.D. 1991, p. 13)

Acknowledgements

I would like to thank Enrico Giannetto for having showed me the starting point of the researches collected in the present dissertation. I would also like to thank him for many informal talks and remarks.

TABLE OF CONTENTS

<i>Foreword</i>	p.	9
FIRST PART: two pathways to Thermodynamics		
<i>1. From Mechanics to Statistics</i>	p.	31
<i>2. Swinging between discrete and continuous theoretical models</i>	p.	49
<i>3. From mechanical models to probability</i>	p.	69
<i>4. The mathematical physics of French engineers</i>	p.	85
<i>5. A Thermodynamic world-view</i>	p.	103
<i>6. From mechanical to thermodynamic equilibrium</i>	p.	119
<i>7. The “free energy” in Physics and Chemistry</i>	p.	133
SECOND PART: Duhem third pathway		
<i>8. Thermodynamics as a new Mechanics</i>	p.	153
<i>9. The “general equations”</i>	p.	171
<i>10. The generalised Mechanics of a “complex system”</i>	p.	191
<i>11. A new “chemical mechanics”</i>	p.	215
<i>12. Looking for a theory of permanent deformations</i>	p.	235
THIRD PART: towards a general theory of transformations		
<i>13. A structural analogy</i>	p.	257
<i>14. Further generalisations and astonishing differences</i>	p.	279
<i>15. From explosions down to mechanical friction</i>	p.	303
<i>Afterword</i>	p.	323
<i>Bibliography</i>	p.	349

Foreword

The roots of complexity in physics

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 of the *Académie des Science* 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 new tradition really emerged in the context of physical sciences, more specifically in the context of mathematical physics.¹ A wide class of phenomena, in some way dealing with heat and 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. Prigogine and Stengers' historical reconstruction would require some refinements and some specifications, but as a simplified outline it does not miss the point. Fourier 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.²

Inquiring into the roots of the theory of complexity requires two specifications, the first involving the history of science, the second involving the history of what nowadays we call epistemology. With regard to history of science, we should remark that 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: the links between Fourier's new approach to physics and the theory of complexity are definitely very loose. With regard to the history of *epistemology*, we

¹ 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."

² 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."

should remark that epistemology as a separate subject or disciplinary curriculum was far beyond the intellectual horizon of the nineteenth century. In some way, physics, history of physics and “epistemology” were mutually entangled aspects of a very sophisticated research practice, which some talented physicists such as L. Boltzmann, H. Poincaré and P. Duhem undertook at the end of that century.

In brief, from the historical and the epistemological point of view, our concept of “complexity”, or the concept of complexity which Prigogine and Stengers referred to, cannot be simply transferred from the second half of the twentieth century back to the early nineteenth century. In order to look for the roots of complexity in physics, the transformation of the theory of heat into Thermodynamics in the middle of the nineteenth century, and the subsequent theoretical researches undertaken around the end of the century appear now far more meaningful than Fourier’s book. In particular, Duhem’s theoretical contribution, at the end of the 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 the following issues:

1. the sensitivity to initial conditions,
2. the impossibility to be reduced to the sum of its subsets,
3. 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.³ In the last decades of the nineteenth century, the theoretical models of gases put forward by Maxwell and Boltzmann let the following question emerge: how can we explain the time-irreversibility of a macroscopic amount of gas in terms of the time-reversibility of the microscopic molecules which are its ultimate components?

Prigogine and Stengers pointed out the deep, intrinsic novelty which thermodynamics introduced into the physical sciences: the behaviour of a system of many particles over time. If mechanical systems could experience different final states depending on the

³ See, for instance, the debate which developed on the review *Nature* between English and German physicists around 1896, or the debate Boltzmann-Zermelo: it is reported in Brush S.G. 1976, pp. 602-40, and in Dugas R. 1959, pp. 185-219.

different initial states, thermodynamic systems seemed drifted towards a macroscopically indistinguishable state of equilibrium.⁴ I find that Prigogine and Stengers' analysis deserves to be further developed, in order to better understand the deep transformations which took place in late nineteenth century physics, and in order to investigate the roots of subsequent transformation experienced by physics in the twentieth century. I would like to inquire, in particular, into an interesting theoretical path underestimated by Prigogine and Stengers: Duhem's path, which led thermodynamics towards a new generalized Mechanics. Following Duhem's *third way* we can fully appreciate one of the most outstanding achievements of late nineteenth century theoretical physics: a new alliance between mechanics and thermodynamics, in order to cope with the complexity of the physical world.

My research will focus on some specific features of Duhem's physics:

- The new conceptual link between mechanics and thermodynamics,
- The attempt at explaining the complexity of the physical world

The time interval is specific as well: I am interested in the decade going from 1886 to 1896. I am trying to follow the intellectual path which led Duhem from an original interpretation of thermodynamics to a great plan for building up a physics of "qualities". We will meet a kind of physics quite difficult to enroll in whatsoever theoretical and meta-theoretical framework.

Two reasons have led me to focus on the decade 1886-1896. In the first place, I have found that the main and most ingenious concepts of Duhem's physics were accomplished before the turn of the century. Moreover, Duhem's meta-theoretical remarks stemmed from Duhem's practice as a physicist, and only subsequently they were expressed in a systematic way, when he dressed the clothes of historian and philosopher of science. In the second place, I would like to stress that those remarks were put forward before the best known 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,

⁴ 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."

but also to experimental and theoretical researches on the new rays and the new particles.⁵

That Duhem's physics has been less studied than his history or his *epistemology* is a matter of fact.⁶ The study of his physics is demanding, because quite sophisticated are both conceptual and mathematical components of his theories. Some 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 would have met the interest of physicists. Moreover, he dignified the tradition of Aristotle's physics, a tradition which was looked upon as a black shadow threatening Galileo's new science. Duhem did not trust in those mythological reconstructions of the birth of modern science. He revived the ancient Greek meaning of the word "physics": not only science of local motion, but a general theory of material transformations, encompassing contemporary physics, chemistry and perhaps some aspects of sciences of life. This new kind of physics, a generalized physics, could account for the complexity of the physical world. Galileo's modern science had to fight against the old physics of qualities, in order to establish itself: the complexity of the physical world had to be neglected in favour of a simplified world. 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 world and carry it into the wider boundaries of a generalized Mechanics-Thermodynamics.⁷

Duhem neither underrated nor refused seventeenth-century scientific revolution; he did not try to turn back, in order to take shelter into ancient philosophies. He aimed at widening the scope of physics: he synthesized his view stating that "we can express physical qualities by means of Algebra". The new physics could not confine itself to

⁵ It seems to me that R. 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."

⁶ Although biographies and studies on Duhem history and philosophy of science have flourished in the last decades, studies on his physics are scanty. Apart from the book published in 1927 by his former doctoral student O. Manville, I can only mention P. Brouzeng 1981 doctoral dissertation (see *Bibliography*). Brouzeng considered Duhem as a "pioneer of thermodynamics of irreversible processes", and considered his theoretical researches as a part of a "chain" connecting "Carnot to Prigogine". (Brouzeng P. 1981, pp. 73 and 157)

⁷ 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 ; ... »

“*local motion*” but had to explain what Duhem qualified “*motions of modification*”: what had been called “*generation and corruption*” in peripatetic words became “*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.⁸

When Duhem undertook his theoretical enterprise, Thermodynamics could already rely on a meaningful history: he saw himself as a developer of a recent specific tradition. More precisely, he looked upon himself as the developer of a “third way” to Thermodynamics. According to Duhem, the *first way* corresponded to the kinetic theory, wherein Thermodynamics was “an application of Dynamics”. 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 way corresponded to a phenomenological approach, wherein Thermodynamics was based on “typical principles”, and was “independent of whatever hypothesis on the nature of heat”. His third way was based on “a different relationship between Dynamics and Thermodynamics”, wherein “Dynamics became a specific instance of Thermodynamics”, and general principle encompassed “all kinds of transformations, from the change of place to the change of physical qualities”.⁹

The first and second pathways to Thermodynamics

⁸ See Duhem P. 1903, in Duhem P. 1992, pp. 199 and 218-9. His more synthetic statement was: “La Mécanique nouvelle ne se contente pas d’être une *Mécanique physique*, elle est encore une *Mécanique chimique*.” Duhem gave a very abstract definition of “quantity of heat”: it was looked upon as a mere “sum of terms without any reference to the concepts of cold and warm”. See Duhem P. 1903, in Duhem P. 1992, pp. 233-4.

⁹ Duhem P. 1894a, pp. 284-5 : « Les fondateurs de la Thermodynamique ont presque tous incliné à faire de cette science une application de la Dynamique ; regardant la chaleur comme un mouvement très petit et très rapide des particules qui constituent les corps, la température comme la force vive moyenne de ce mouvement, les changements d’état physique comme des modifications dans les éléments caractéristiques de ce mouvement, ils ont tenté de déduire les théorèmes de la Thermodynamique des théorèmes de la Mécanique rationnelle ; ... Beaucoup de physiciens ont cherché à rendre la Thermodynamique indépendante de toute hypothèse sur la nature de la chaleur ; ils ont essayé d’établir non sur des théorèmes emprunté à la Mécanique rationnelle, mais sur des principes qui lui soient propres ; ... 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 communes tous les changements d’état des corps, aussi bien les changements de lieu que les changements de qualités physiques. »

In the 1820s, 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 heat into mechanical work. 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. The most striking difference between Mechanics and Thermodynamics was perhaps the role of initial positions and velocities. In Mechanics, that information led to a predictable time evolution and trajectory. In Thermodynamics, the system forgot that information: whatever starting point of non-equilibrium transformed into the same condition of equilibrium.¹⁰

In some papers published since the 1850s, Clausius abandoned Carnot's idea that heat was conserved, and showed that the absolute temperature of a gas was proportional to the translational kinetic energy of its molecules. He put forward the second law of thermodynamics and associated to it a new physical concept, the *entropy*. 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.¹¹ 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 equilibrium state. He looked for a law which could also describe the evolution towards that equilibrium. He was strongly influenced by Darwin's researches on the 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. Statistics and probability did not

¹⁰ A historical reconstruction of this stage of Thermodynamics can be found, among many others, in Duhem P. 1895c, pp. 401-18, and Brush S.G. 1976, Book 2, pp. 568-71. Even though they have in common the fact of being both physicist and historians, Duhem and Brush put forward different interpretations of the history of thermodynamics, apart from the obvious time lag between their historical researches. There is not something like a history of Thermodynamics: there can only be many histories of Thermodynamics.

¹¹ See Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, pp. 377-83; Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 27-45.

represent a sort of contrivances but the suitable intellectual tool to describe the evolution of a great population of molecules.¹²

Boltzmann, following Maxwell's tracks, introduced probability in physics in a new fundamental way: not in order to attain some useful approximation but as an intrinsic property of the system. Probability gained a new epistemic role, not so different from the role of the recently stated principles of conservation.¹³ In Boltzmann's representation, the motion of molecules involved both continuous paths and discrete collisions. In some way, two different traditions were at stake: the Newtonian tradition of laws of motion, on the one hand, and the Cartesian and Leibnitzian tradition of collisions and laws of conservation, on the other hand. The behaviour and the evolution of the whole system required the complex interplay between these traditions. Beside the conceptual tension between continuous and discrete representations of physical events, other tensions or dichotomies were involved: macroscopic versus microscopic representations, reversible versus irreversible behaviour of physical systems, and eventually determinism versus probability.¹⁴

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.¹⁵ As an instance of the new horizons opened by Thermodynamic I would like to quote a Boltzmann's lecture held in 1886, wherein he imagined a body moving in a definite direction with a given velocity as an "infinitely improbable configuration of energy". According to that view, "visible motion behaves like heat of infinitely high

¹² See, for instance, Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 316-19, 322-461, and Boltzmann L. 1877, in Boltzmann L. 1909, II Band, pp. 167-90 e 215-23. On Boltzmann's *Darwinism*, see 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.

¹³ See Prigogine I. and Stengers I. 1986, p. 194: "L'innovation consistait à introduire la probabilité en physique et cela, non pas à titre de 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"

¹⁴ The conceptual tension between determinism and probability should not be interpreted as a contradiction. See Cassirer' analysis in Cassirer E. 1936, p. 129: "Die geschichtliche Betrachtung sollte nur das eine lehren, dass zwischen den Begriffen 'Zufall' und 'Gesetzlichkeit' keineswegs, wie oft angenommen wird, ein Verhältnis der kontradiktorischen Gegensätzlichkeit besteht."

¹⁵ With regard to the criticism about Boltzmann theory, in particular Loschmidt criticism, Zermelo criticism, and the debate between Boltzmann and british physicists, see 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. See also footnote 3.

temperature”, which “can be completely transformed into work”. In some way, Mechanics became an extreme case of Thermodynamics: this sounds quite astonishing when we notice that Boltzmann is considered by historians an upholder of the so-called *mechanical world-view*.¹⁶

A different theoretical pathway was undertaken by the Scottish engineer M. Rankine, and by the French engineers F. Reech and R. Massieu: they tried a highly abstract, mathematical re-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 are definitely less known. Reech was Navy engineer and director of the *École du Genie Maritime*; Massieu was mining engineer and professor at Rennes university. The role of Reech was discovered in the 1960s by the mathematical physicist and historian of physics A.C. Truesdell. Although mentioned by Gibbs and Duhem, Massieu is not generally mentioned, apart from “Massieu functions” mentioned in some treatise of statistical mechanics and thermochemistry. He was able to demonstrate that some mechanical and thermal properties of physical and chemical systems could be derived from his two “characteristic functions”. 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”.¹⁷

Gibbs and Helmholtz developed that abstract re-interpretation of Thermodynamics, and relied on a 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”, J.W. Gibbs showed that Massieu’s 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 put forward the

¹⁶ Boltzmann L. 1886, in Boltzmann L. 1974, p. 22, and Cassirer E. 1936, pp. 95-6.

¹⁷ See Massieu R. 1869a, pp. 859-60, Massieu R. 1869b, pp. 1058-60, and Massieu R. 1876, pp. 3, 8-19, and 25-35. See Rankine M. 1855, in Rankine M. 1881, pp. 213-4. Massieu published two short papers in 1869 and a longer one in 1876 on his “Fonctions caractéristiques”. The name of “Massieu” does not appear in the *Dictionary of Scientific Biography* but can be found in a modern treatise (Balian R. 1992, § 5.6, “Entropy and Massieu functions”). He is mentioned in Perrot P. 1998, p. 190, wherein it is said that “Massieu function ... is now of only historical interest”. He is mentioned also in Klein M.J. 1983, p. 161, footnote 35, and Kragh H. 1993, pp. 403-31.

concept of “free Energy”: it was the variation of the free energy, rather than the whole delivery of heat, to correspond to the actual direction of chemical transformations.¹⁸

Duhem third pathway

This was Duhem’s scientific background when he published *Le potentiel thermodynamique et ses applications à la mécanique chimique et à la théorie des phénomènes électriques* in 1886. In the first pages of the book he showed that entropy and volume of a physical system corresponded to some derivative of a potential Φ . Other derivatives allowed him to obtain coefficient of dilatation and compressibility, as well as the specific heat at constant pressure.¹⁹ Since 1886, Duhem’s design of a new physics evolved through three subsequent steps:

1. the cross-fertilization among mechanics, thermodynamics and chemistry,
2. the rephrasing of Thermodynamics according to the *syntax* of Analytical Mechanics, and the foundation of Mechanics on the principles of Thermodynamics,
3. the unification of “local motion”, thermal phenomena, electromagnetic phenomena, and transformations of matter in the context of a generalized Mechanics.

What in Gibbs was a development of a mathematical analogy, became in Duhem a wide-scope program of research. In 1891, in the essay “Equations générales de la Thermodynamique”, he generalized the concept of “virtual work” under the action of “external actions” by taking into account both mechanical and thermal actions. In 1894 the design of a generalized Mechanics based on thermodynamics was further developed: ordinary mechanics had by now become “a particular case of a more general science”.²⁰

In 1896, in the very long essay “Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques”, he proceeded to a detailed reconstruction of some physical and chemical processes neglected or underestimated by physicists

¹⁸ See Gibbs J.W. 1875-1879, pp. 55-6, 62-9, 87-93, 115-6, 138, 184-5, 209-14, and 354-5. See Helmholtz H. 1882, p. 960.

¹⁹ Duhem P. 1886, pp. 11-13.

²⁰ See, for instance, Duhem P. 1894a, p. 285 : « [...] 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 des tous les phénomènes physiques à l’étude du mouvement ; ... ».

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.²¹ In the meanwhile, starting from 1895, in a series of essays under the common title "Les déformations permanentes et l'hysteresis", he had began to develop a theory which took into account the permanent modifications of bodies. This ambitious design was hindered by many difficulties, both theoretical and experimental.

Even though I have stated that I am focusing on Duhem's physics, I am aware that theoretical physics, history of physics and meta-theoretical remarks are mutually interconnected in Duhem's actual praxis. In his papers and books the historical awareness is always a fundamental feature. In his search for a new generalized Mechanics, Duhem acknowledged the existence of different stages in the history of Mechanics, and the necessity of those stages. They were fruitful and meaningful, even though, at the end of the nineteenth century, science called for a new stage, namely his generalized Mechanics-Thermodynamics. His design of re-interpretation of Aristotelian physics could be pursued only by a scientist endowed with a deep knowledge of physics, a wide knowledge of history, and a subtle meta-theoretical sensitivity.²²

Both historians and philosophers of science have made use of scholarly words in order to describe Duhem's scientific heritage: some words are *energetics*, thermodynamic view of nature, anti-mechanism and *conventionalism*. Are them suitable words, or merely "consolations for specialists"?²³ With regard to the first label "energetics", we can notice that Duhem gave it the meaning of generalized Thermodynamics, rather than the meaning of a world-view or a general meta-theoretical commitment. We find a

²¹ Duhem P. 1896, p. 205 : « 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 introduites 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'Énergétique : les divers changements de propriétés d'un système ne se réduisent pas au mouvement local ; ... »

²² In the time span we are interested in, Duhem published some papers on history and philosophy of science in the Belgian journal *Revue des questions scientifiques*. See Duhem P. 1892b, 1893c, 1893d, 1893e, 1894c, 1896b.

²³ I am referring to Feyerabend's famous essay: "Consolations for the Specialist", in Lakatos I. and Musgrave A. (eds.) 1970, *Criticism and the Growth of Knowledge*, Cambridge University Press, Cambridge UK, pp. 197-230. With regard to the debate on the *rate* of conventionalism, realism, "phenomenism", or "phenomenalism" in Duhem, see, for instance, Maiocchi R. 1985, second chapter, Redondi P. 1978, first chapter, Stoffel J-F. 2002, second and third part, ...

remarkable conceptual distance between Duhem and some upholder of “energetics” like G. Helm and W. Ostwald. If Duhem developed a sophisticated mathematical theory of thermodynamics, the latter insisted on the principle of conservation of energy as the sole foundation of physics. In particular, Ostwald developed a physical world-view wherein, in Ostwald’s words, “the concept of matter, which has become indefinite and contradictory, has to be replaced by the concept of energy”.²⁴ In no way the name of Duhem can be associated to that kind of “energetism”.

With regard to the second label “thermodynamic world-view”, we can notice that in reality Duhem tried to found all physics on the two principles of Thermodynamics but, at the same time, translated thermodynamics into the language of analytic Mechanics. We could say that we find in Duhem both a mechanical foundation of thermodynamics and a thermodynamic foundation of mechanics. I find that this label would suit more Rankin than Duhem. With regard to the third label “anti-mechanism”, we can notice that 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 physical phenomena. An instance of these analogies can be found in Duhem’s analysis of chemical “false equilibrium”, wherein the comparison with the motion along an inclined plane with friction is put forward.²⁵

With regard to the fourth label “conventionalism”, we should distinguish the different nuances of meaning which we find in primary and secondary literature. But, even though this analysis could be undertaken here, I would find it pointless. The fact is that Duhem had a dynamical conception of science, a conception which have always poked fun at historians and philosophers who have tried to classify him. We can notice that his conception had much in common with Boltzmann’s conception, a physicist who undertook an opposite way to thermodynamics, wherein specific mechanical models of

²⁴ See Ostwald W. 1896, pp. 159-60: “Ihren schärfsten Ausdruck hat dies erkenntnisstheoretische Postulat durch meinen Hinweis erhalten, dass der unbestimmt und wider spruchsvoll gewordene Begriff der Materie durch den der Energie zu ersetzen ist, da nur auf solchem Wege die Uebereinstimmung zwischen dem, was wir durch unsere Formeln zum Ausdruck bringen, und dem, wovon wir zu reden pflegen, hergestellt werden kann.” W. Ostwald held the sole German chair of physical chemistry, at the University of Leipzig, from 1887 until his retirement. On the debate on energetism, see Helm G. 1895, and Helm G. 1898; see also McCormach R., Jungnickel C. 1986. Vol. II, p. 220, and Harman P.M. 1982, p. 147.

²⁵ See Duhem P. 1896, p. 8: “Les false équilibres que l’ont rencontre en mécanique chimique ont leurs analogues parmi les équilibres purement mécaniques.” The analogy is developed in pp. 8-9.

heat were involved.²⁶ I find that some epistemological analogies between Duhem and Boltzmann are at least as meaningful as those between Duhem and Poincaré, Mach or Hertz.²⁷

I would not like here to enter the land of *epistemology* in its widest sense: I would like to enter the narrower land of Duhem's Thermodynamics, and let specific theoretical, and meta-theoretical issues stem from it. The fact is that much literature has been published on Duhem as 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 about physics.²⁸

At the end of an inquiry into ten years of Duhem's theoretical researches, we should wonder: what remains now of those theories? Have they been fruitful? I have tried to answer this question in the *Afterword* to the present dissertation, but I find that some specifications are required now.

In the first place, I am aware that the scientific fruitfulness can be found at different levels: the level of the specific theoretical models, the level of the general theoretical streams, or at the level of meta-theoretical commitments. In the tradition of theoretical physics, just emerged in the last decades of the nineteenth century, we should distinguish these different levels. The first level corresponds to the choice of equations, of the class of phenomena under investigation, and of the specific hypothesis and deductions applied to that class of phenomena. The second level corresponds to the choice of the more general principle and hypotheses, and to their interplay. Eventually, the third level corresponds to features and aims of the scientific enterprise. I must offer some instances. In the case of Duhem's last essay, investigated in the last chapters of

²⁶ 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 cannot be looked upon as "incontrovertibly established truths", for they are based on hypotheses which "require and are capable of continuous development". See Boltzmann L. 1905, pp. 592-5. We must point out that, at the same time, he could not rely on pure "mathematical phenomenology". See Boltzmann L. 1899, in Boltzmann L. 1974, p. 95.

²⁷ For the latter analogies, see, for instance, Maiocchi R. 1985, chapter V, "Duhem nella cultura del suo tempo: alcuni raffronti", pp. 293-344.

²⁸ Jaki's scientific biography, for instance, devotes only one sixth of its content to Duhem's physics: see Jaki S.L. 1984, pp. 259-318. We can find a reliable summary of Duhem's physics in Manville already mentioned book. Roughly thirty pages of the book are devoted to the list of Duhem's papers and books. Among that overshadowing heritage, my dissertation concentrates on the following texts belonging to the span of a decade: Duhem P. 1886, Duhem P. 1888, Duhem P. 1891, Duhem P. 1892a, Duhem P. 1893a, Duhem P. 1893b, Duhem P. 1894a, Duhem P. 1894b, Duhem P. 1895a, Duhem P. 1895b, Duhem P. 1896a.

the present dissertation, the peculiar choice of Lagrangian equations, the peculiar interpretation of “viscosity” and “friction”, and the peculiar choice of phenomena to be described (for instance “false chemical equilibrium”), are instances of first-level options. That mechanics, thermodynamics and chemistry could experience a unified mathematical processing, or that the natural world should be described by continuous models, are instances of second-level options. As an instance of Duhem’s third-level option I could mention his commitment to overcome Galilean reductionism, and to open physics to the complexity of the physical world, but also the awareness of the intrinsic historicity of the scientific enterprise.²⁹

Duhem in context: historical and historiographical remarks

I will inquire into the net of general hypotheses, specific models and mathematical tools which emerged in the last decades of the nineteenth century and which found its more sophisticated expression in the texts of some outstanding natural philosophers and physicists: Maxwell, Boltzmann, Rankine, Gibbs, ... apart from Duhem himself. I have qualified them in a double way, as natural philosophers and as physicists, for a specific reason. What we call physics, namely a definite field of knowledge and a definite professional appointment after a definite academic training, was an outcome of a historical process which took place just in the last decades of the nineteenth century.³⁰

I will concentrate my inquiry into the field of theoretical physics, rather than physics in general, because theoretical physics was the field where Duhem excelled in. In a wider perspective, if the emergence of physics as a definite academic discipline was a heritage of late nineteenth century, the emergence of theoretical physics was the most original element of that heritage. I will take into account both equations and philosophical reflexions, in particular specific mathematical models and more general theoretical and meta-theoretical remarks. In the perspective of the history of science, the fruitful alliance between the tradition of mathematical physics and the most speculative

²⁹ This historiographical sketch suits the specific season of theoretical physics we are dealing with, and perhaps the decades going roughly since 1880s till 1920s: it cannot be extended upon a longer time span.

³⁰ On the process of specialization and professionalization taking place at the end of the nineteenth century, see, for instance, Ross S. 1964, p. 66. In Italy and Great Britain, for instance, physics was also practiced by scholars appointed to chairs of mathematics.

side of the tradition of natural philosophy was perhaps the most distinctive hallmark of late nineteenth century theoretical physics.³¹

To describe what really theoretical physics was in that time span, is a very demanding task, because both intellectual and institutional events were involved. I only confine myself to single out some distinctive feature, in order to better understand the context wherein Duhem undertook his scientific practice. Theoretical physics emerged in the last decades of the nineteenth century as a fruitful and original alliance between two different traditions: the tradition of applied mathematics and the tradition of natural philosophy. In particular, the tradition of Lagrange's and Hamilton's mathematical physics merged with the most speculative side of early nineteenth century philosophy of nature. Even though the academic recognition of theoretical physics was achieved only in German speaking countries, and in a very contradictory way, theoretical physics as an actual new practice in physics can also be found in France, Great Britain and then in Italy. We can mention Duhem and H. Poincaré in France, H. Hertz, M. Planck and L. Boltzmann in German speaking countries, J.J. Thomson and J. Larmor in the British islands, and V. Volterra in Italy.

Some of them had been trained as mathematicians; some others were engineers. From the academic point of view, Poincaré was a mathematician. Duhem considered himself physicist and mathematician: after the rejection of his doctoral dissertation, the new one was accepted in the section of mathematics, and his physics was appreciated by mathematicians rather than by physicists. J.J. Thomson and J. Larmor had passed the highly selective Cambridge Mathematical Tripos, even though J.J. Thomson had gained his first degree as an engineer. V. Volterra was a mathematician. We cannot forget that, among the first physicists who built up theoretical thermodynamics, M. Rankine and R. Massieu had been trained as engineers, and held chairs of engineering in Scotland and France.

The main hallmark of late nineteenth century 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

³¹ On the emergence of theoretical physics at the end of the nineteenth century, see McCormach R. and Jungnickel C. 1986, vol. 2, pp. 33, 41-3, 48, and 55-6, and Bordini 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.

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 refer to the same kind of experiments: the difference among them could be found just at the conceptual level.³² Conversely, a given set of phenomena could be consistently described by different theories making reference to different conceptual models. The history of electro-dynamic theories in the second half of the nineteenth century had shown the relevance of the debate between the conceptual models of action at a distance and contiguous action. Moreover, the emergence of theoretical physics corresponded to a new sensitivity to meta-theoretical issues. Physicists committed themselves to explicit designs of unification, and explicit methodological remark, as well as explicit questioning of the foundations of physics. In that season, all these cogitations were looked upon as intrinsic aspects of the scientific practice. Scientists did not entrust philosophers with the reflection on aims and methods of science any more: meta-theoretical remarks began to emerge from inside science, and not addressed to science from the outside.³³

We have many instances of that widening of horizon in physics. An early instance was offered by Rankine design of abstract generalisation of Thermodynamics. In the last decades of the century, we find Larmor and the theoretical and meta-theoretical role played by invisible entities like aether. We find Poincaré and the legitimate use of a plurality of theories in the interpretation of a given set of phenomena. Eventually we find Duhem and the subtle interplay between mathematical, empirical, conceptual, historical and methodological aspects. What all these physicists had in common was a

³² It seems to me that a similar point of view has been put forward in Giannetto E. 1995, pp. 165-6.

³³ See Cassirer E. 1950, pp. 82-4: “From the middle of the nineteenth century onward the demand for reflective criticism in the natural sciences was urged with ever mounting emphasis. [...] 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.”

sort of double attitude towards their own practice: there was an original combination of confidence and disenchantment about science.³⁴

With regard to the meta-theoretical debates, two different models of scientific knowledge were at stake. On the one hand, the attempt at going beyond the shield of visible phenomena, in order to catch their true microscopic nature. On the other hand, only mathematical representations, without pursuing whatsoever kind of subtler explanation. We find the Britons Larmor, J.J. Thomson, G.F. FitzGerald and O. Lodge, but also Lorentz and Boltzmann deployed on the first front. On the second front we find G. Kirchhoff, E. Mach, G. Helm, W. Ostwald and Duhem. Among those who swung from the one to the other meta-theoretical option we find H. Hertz and then Planck, who followed Rankine, J.C. Maxwell, R. Clausius and Helmholtz's similar attitude. Poincaré looked at the two complementary attitudes with Olympic detachment. Roughly speaking, Duhem belonged to the set of phenomenologist physicists, but the role of theory and meta-theory was so important in his actual scientific practise that we should not put him beside Mach, Helm or Ostwald without the above specifications on Mechanism and Energetism. We could associate him to Hertz, but we could find in his conception of science even meaningful analogies with Boltzmann's historical and evolutionary conceptions.³⁵ This could sound quite astonishing, when we consider that Boltzmann's route to Thermodynamics through discontinuous and microscopic mechanical models was far from Duhem's route, which aimed at an abstract generalisation, wherein Mechanics of continuous media had to merge with Thermodynamics. Nevertheless, this astonishingly gap can be properly understood if we distinguish the first and second level from the third one.

We can find deep differences between Duhem and Boltzmann on the first and second level, but some meaningful analogies on the third level. In the late nineteenth century, at the third or meta-theoretical level, the debate involved Helm against Planck, and FitzGerald against Ostwald.³⁶ Boltzmann and Poincaré managed to clearly describe the

³⁴ 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.

³⁵ 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.

³⁶ In Germany the debate was quite sharp, mainly around 1895, when the energetists were the chief characters of the annual conference of German scientists and physicians held in Lübeck. One of those characters, G. Helm, in a book published in 1898, pointed out the relevant features of the more radical energetism. The debate continued after

two meta-theoretical attitudes: *explanations* by means of specific mechanical models, or *descriptions* in terms of a formal language. Duhem took part to the debate with an original point of view. He did not appreciate the mechanical models, and undertook a wide design of generalisation of physics, relying on the explanatory power of a generalised Analytic Mechanics. In some way, he pursued a sort of sophisticated, abstract Mechanism, quite different from the Mechanism of British physicists. We could say that his Mechanism was a sort of structural Mechanism, far beyond whatsoever kind of mechanical model. He spoke of his design in terms of Energetics, but even his Energetics was quite different from Helm or Ostwald's. It was quite close to Rankine Energetics, in the sense of a generalised, abstract Thermodynamics.

The emergence of theoretical physics was accompanied by deep transformations in the field of physical sciences. 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.³⁷ In reality, from 1860s on, physics had been experiencing two important transformations: in simplified terms, we could say that the first was internal and the second external to the scientific practice. The former consisted in the mathematisation and systematisation of previously scattered researches on heat and electricity. The latter consisted in a sort of social success of science: science had finally managed to realize part of Bacon's dream, and the myth of scientific progress was emerging.

We should analyse the two transformations separately. With regard to the former (*internal*) transformation, 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

the conference, through the pages of *Annalen der Physik*, between 1895 and 1896. See McCormmach R. and Jungnickel C. 1986, vol. 2, pp. 219-20, and Cassirer E. 1950, pp. 96-7. For a short account of the complex conceptual net involving Boltzmann, Ostwald and Planck's approaches to thermodynamics see 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.

³⁷ Kuhn's historiographical theses are too 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.

outset with the Newtonian idea of force”. In other words, the new concepts of “electromagnetic field” and “entropy” challenged the explanatory patterns developed since the end of the seventeenth century.³⁸

With regard to the latter (*external*) transformation, I must remind the reader that the last decades of the nineteenth century saw the spread of electromagnetic technologies: indeed those technologies managed to improve everyday life of ordinary people. Not only did electric light inside houses and on the roadside of the towns modify the landscape of urban life, but 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 the electric energy consisted also in its versatility and portability: since the end of the 1860s, the world, mountains and ocean included, was crossed by hundred thousand miles of telegraph cables. It was in that social and technological context that the myth of the scientific progress emerged. At the same time, the wider-scope myth of the social progress triggered off by the scientific progress also emerged.³⁹

This is the context wherein Duhem developed his researches: starting from a bold design of generalisation and unification of physics, he subsequently arrived at original theses on meaning and limitations of the scientific enterprise. The specific epistemological remarks, together with the more general philosophical cogitations, he had began to express in the 1890s were subsequently collected in the famous book he published in 1906, *La théorie physique, son objet, et sa structure*. It is worth noticing that, in the last decades of the nineteenth century, debates on the relationship between science and theology also took place, and the second Principle of Thermodynamics brought a fascinating topic to that debate. Duhem did not appreciate the cosmological interpretations of the two Principles of Thermodynamics, nor he found interesting the cogitations on the relationship between energy conservation and free will. He was a firm believing and, at the same time, “an independent mind”: he disliked transforming

³⁸ Cassirer E. 1950, p. 85. The concept has been recently revived by Renn J. and Rauchhaupt U. 2005, pp. 31-2.

³⁹ 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.

scientific contents into apologetic arguments, and always insisted on “a sharp separation between science and faith”.⁴⁰

⁴⁰ See Kragh H. 2008, pp. 113-7. I find Kragh brief reconstruction substantially exact. 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)

FIRST PART

Two pathways to Thermodynamics

1. From Mechanics to Statistics

In September 1859, Maxwell, 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. Then he sent the paper to the *Philosophical Magazine*, a scientific journal which had already hosted dynamical theories of matter and heat. The paper, “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. 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 by a theoretical model involving microscopic particles in motion “with uniform velocity in straight lines”. In that model, the pressure of the gas was the effect of the strikes of the particles “against the sides of the containing vessel”.

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 deepen Clausius’ theoretical investigation, which should have been 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”.¹

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. According to Maxwell’s view, the purely kinetic model could have been replaced by a *dynamical* model. In other words, instead of “hard, spherical and elastic” particles in motion, we could imagine particles as “centres of forces”. The fact is that the two models stemmed from very different conceptual models: matter and motion on the one hand, and matter

¹ Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p. 377.

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 forces which were “insensible except at a certain small distance” but, at a smaller distance from a particle, a force “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 qualitative. Then he proceeded to develop “the assumption of perfectly elastic spherical bodies”.²

The subject is structured 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 lies between x and $x+dx$, where $f(x)$ is the fraction of such particles, N is the total number of particles and x, y, z are the Cartesian components of the 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”.³ According to that hypothesis, Maxwell could write 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 $z+dz$:

$$N f(x) f(y) f(z) dx dy dz.$$
⁴

² Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p. 378. Clausius had already shown that, in case of non-spherical particles, “the rotatory motion of the system” should have been taken also into account, and rotation would “store up a certain proportion of the whole *vis viva*”. In the paper, he treated the more general case in the short third part, “On the Collision of Perfectly Elastic Bodies of any Form”. See *Ibidem*, p. 405.

³ The fact is that the claimed independence among the components does not hold good: the conservation of momentum and energy does not allow 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: “Maxwell assumed in his 1860 paper that the probability of a molecule having a certain value of the x -component of velocity is not affected by knowledge of its y -component of velocity. He did not recognize that this assumption cannot be true in a finite system with fixed total energy (if one component of velocity is so large that it corresponds to nearly the entire kinetic energy of the system, then the other components cannot have similarly unrestricted values).”

⁴ Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p. 380.

Another simplification arose from the rotational symmetry in the space of velocities: the law of velocities distribution must be insensitive to the direction of velocities: a sort of isotropy in the space of velocities let the distribution of velocity depend only on the *length* of the vector velocity.

“But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2).$$

Solving this functional equation, we find

$$f(x) = C e^{Ax^2}, \quad \phi(r^2) = C^3 e^{Ar^2}.”$$

The constant A must be negative, otherwise the number of particle 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.”⁵

Apart from the soundness of the hypotheses Maxwell had assumed, in which sense is 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”.⁶ In any case, the deduction of the mathematical law of distribution did not involve specific mechanical laws as, for instance, the laws of elastic collisions. It involved only some global properties or symmetries of a huge number of particles.

Nevertheless, when in the “Proposition VI” Maxwell tried to deduce one of the effect of the drift towards the equilibrium, namely the uniform distribution of *vis viva* between two sets of particles having two different kinds of mass, he resorted to the laws of mechanics. Let P the mass of the first kind and p the average velocity in the first set of particles; let Q the mass of the second kind and q the corresponding average velocity. After the impact between two particles of different kind, masses and velocities became P', p', Q' and q' . In few passages Maxwell showed that, after the first impact,

$$Pp'^2 - Qq'^2 = \left(\frac{P-Q}{P+Q} \right)^2 (Pp^2 - Qq^2).$$

Since the term involving the masses $\left(\frac{P-Q}{P+Q} \right)^2$ is less than 1, the expression $(Pp^2 - Qq^2)$ undergoes a progressive decrease.⁷

⁵ Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 381.

⁶ Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 383.

⁷ Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 383.

We see that a global macroscopic approach, relying on statistical laws, was put forward alongside a local microscopic approach, relying on mechanical laws.

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.⁸ The subject was introduced by nine pages of general remarks and historical notes on matter, elasticity and kinetic theory. A series of short section followed, ranging over 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 move along “sensibly rectilinear” paths before entering “the sphere of sensible action of the neighbouring molecules”. Starting from this theoretical model, Maxwell thought to be able to account for the law of gases and the known physical and chemical phenomena.

“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 mechanical 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.”⁹

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

⁸ In 1860 he 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. In 1871 he would have accepted the offer from Cambridge to become the first Professor of Physics of Cavendish Laboratory.

⁹ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 27.

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.”¹⁰

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 is the process leading to uniform, or completely disordered, spatial distribution of molecular velocities. This is a very important issue, and all Maxwell’s words and passages deserve to be carefully quoted. He started from a causal relationship: if “the velocities ... were independent of one another”, then “the pressure at any point of the gas need not be the same in all directions”. This is a relationship of the kind: if A, then not necessarily B follows. But, Maxwell wrote, “we must suppose some cause equalizing the motion in all directions” in order to account for “the observed equality of pressure in all directions”. In other words, B necessarily happens, and we need a mechanism bringing about the equalisation. The mechanism would be

¹⁰ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 29. In the following decade Maxwell would have 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 doctrine 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 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. (Maxwell J.C. 1873, p. 437, and Maxwell J.C. 1875, in Maxwell J.C. 1890, vol. 2, pp. 470-1)

nothing else but that “deflection of the path of one particle by another”. The first conditional sentence is not so definite from the logical point of view. If it had the simple logical structure $A \rightarrow \text{not}(B)$, we should conclude that $B \rightarrow \text{not}(A)$, namely molecular velocities cannot be “independent” of one another. But this is not Maxwell’s conclusion: he does not state that velocities cannot be independent. It does not seem that Maxwell were interested in putting forward a clear, definite chain of logical statements. We cannot specify what definite logical relationship Maxwell held among equalisation of the pressure in all directions, uniform spatial distribution of velocities, and “independence” of velocities of different molecules. From the physical point of view, the question is: uniformity of pressure seems consistent with mutual independence of molecular velocities. This independence should be made consistent with the existence of a precise mathematical law of interaction (“the repulsion is inversely as the *fifth* power of the distance”) among the molecules. At that stage, Maxwell did not inquire into these logical and physical consequences of his model. Moreover, pressures could be equalised “only in the case of a gas at rest”; if it were not the case, the process of equalisation would give rise to “the phenomena of viscosity or internal friction”.¹¹ 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 gas as a whole and the microscopic scale of every couple of interacting molecules.

Another query involved the role of the vessel containing the gas. It was assumed that the gas deserved a microscopic analysis, whilst the vessel did not. In other words, the gas was assumed as a complex set of microscopic components whilst the vessel as a simple geometrical object. But, consistently with the hypothesis that matter, whether solid or gaseous, has got a microscopic structure, even the vessel would deserve such a detailed, microscopic investigation. Dynamical or purely kinetic interactions between the molecules of the gas and the molecules of the vessel should be taken into account. Maxwell noticed that it was the existence of a huge number of molecular scattering that allowed the theorist to assure the *gaseous* behaviour of the gas itself, and to neglect the detailed behaviour of the sides of the vessel. In order to synthetically discuss the query,

¹¹ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p 30.

Maxwell put forward a very peculiar model of gas. He imagined a rectangular vessel “with perfectly elastic sides”, with molecules inside having “no action on one another”: molecules cannot collide with each other or “cause each other to deviate from their rectilinear paths”. In such a model, the pressures on the different sides of the vessel would be “perfectly independent of each other”, so that the vessel could experience different tensions in different direction of space. In some way, the gas would not behave as a fluid but as “an elastic solid”.¹²

In this model, the vessel cannot be looked upon as a mere geometrical entity any more. It would be a *physical* entity, and its complex interaction with the gas could not be neglected. The “rigidity”, or the elastic reaction of the system gas-vessel, Maxwell 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 cannot be an instantaneous process: the transient inequality of pressure is exactly what “constitutes the phenomenon of viscosity”. Another effect of molecular collisions, “when molecules of different kinds are present”, is the equalisation of *vis viva* among the different kinds. He reminded the reader about his 1860 paper, where he had shown that the subsequent impacts between molecules of different masses lead to the equalisation of their kinetic energies.¹³

In the last two pages of introductory remarks, with his usual synthetic but conceptually dense approach, Maxwell devoted some passages to the concept of “molecule”. He held that, in his model of gas, molecules are “those portions of it which move about as a single body”. Maxwell was aware that that very general definition could only be considered as a first stage: many different, specific models could be drawn from it. Among them, there were the models of molecules as “mere points”, or “pure centres of force endowed with inertia”. But molecules could have an internal structure, as 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

¹² With regard to the representation of a gas as a solid, Brush, Everitt and Garber remarked that we expect 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 integrated connection of gas and vessel, not the gas in itself, behave like a solid. Moreover, the vessel must be looked upon as a physical (“let the walls be flexible and rough”) rather than a geometric entity.

¹³ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 32-3.

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 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 redistribution of these two components of energy. In the model of molecules as centres of force, the second component cannot come into play, but in the other models it cannot be neglected. Nevertheless Maxwell thought he could resort to a Clausius’ previous hypothesis, namely that the two components had, on average, a well definite ratio “depending on the nature of the molecules”.¹⁴

In the following sections, Maxwell proceeded to discuss the interactions between couples of molecules, and the law ruling the distribution of velocities among the molecules. When compared to his previous paper (1860), we see that, in 1867, Maxwell put forward a completely different demonstration, but he retained the same result, and made reference to a similar property of mutual independence among the velocities of the molecules.¹⁵

In the first section, “On the Mutual Action of Two Molecules”, he assumed explicitly that molecules are “simple centres of force”, and that the forces mutually acting on a couple of them make them describe “a plane curve” about their centres of mass. This is not, of course, the purely kinematic model put forward in 1860: now intermolecular forces are at work. The dynamical analysis starts from two molecules travelling on straight lines, then undergoing a sudden repulsive force, and finally, if their velocities allow them “to carry them out of the sphere of their mutual action”, departing from the

¹⁴ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 33-4.

¹⁵ On the difference between the conditions of independence in Maxwell’s 1860 and 1867 papers, see Brush S. 1976, book 2, pp. 587-8: “The number of encounters of molecules having two particular values of the velocity vector is then assumed to be proportional to $n_1 n_2$, the product of the numbers having those values separately; but Maxwell does not explain why such an assumption of independence of the velocities of two molecules is any more acceptable than his previous assumption of the independence of different components of the velocity of the *same* molecule. There is one important difference which becomes clear only in Boltzmann’s later work: Maxwell’s second assumption makes it possible to describe an irreversible time evolution of the velocity distribution function.”

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 asymptote of each molecule and the line of apses.¹⁶ This is a typical mechanical analysis of the motion of two bodies ruled by a central force. Besides the geometrical parameter Maxwell introduced a physical parameter, the relative velocity 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: the form of the function depended on the law of force between the molecules.¹⁷ A detailed geometrical and kinematical analysis followed:

“Let V be the velocity of M_1 relative to M_2 , then the components of V are

$$\xi_1 - \xi_2, \quad \eta_1 - \eta_2, \quad \zeta_1 - \zeta_2.$$

The plane of the orbit is that containing V and b . Let this plane be inclined ϕ to a plane containing V and parallel to the axis of x ; then, since the direction of V is turned round an angle of 2θ in the plane of the orbit, while its magnitude remains the same, we may find the value of ξ_1 after the encounter, Calling it ξ_1' ,

$$\xi_1' = \xi_1 + \frac{M_2}{M_1 + M_2} \left\{ (\xi_2 - \xi_1) 2 \sin^2 \theta + \sqrt{(\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2} \sin 2\theta \cos \phi \right\} \quad (1).''^{18}$$

Similar expression should be written for the other components of M_1 velocity. 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

¹⁶ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 35.

¹⁷ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 35-6.

¹⁸ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 36.

of force”. As I have already noticed, the model was not a purely kinetic one: in some way, the latter was an approximation of the former. Maxwell 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 can be looked upon as free molecules. We can neglect, 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.¹⁹

In the following section, “On the Mutual Action of Two Systems of Moving Molecules”, Maxwell imagined two kinds of molecules in the same vessel. His approach was statistical rather than mechanical: following the same path of his 1860 paper, he introduced a function of velocity $f(\mathbf{v})$ 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. He was looking for a simple mathematical expression representing the number of particles of the first kind having velocities in the infinitesimal three-dimensional interval lying between $[\xi_1; \xi_1 + d\xi_1]$, $[\eta_1; \eta_1 + d\eta_1]$ and $[\zeta_1; \zeta_1 + d\zeta_1]$. Maxwell expressed that number by means of the required function $f(\mathbf{v})$, in the following way:

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

A similar expression can be written down for the number of molecules of the second kind having velocities in the interval lying between $[\xi_2; \xi_2 + d\xi_2]$, $[\eta_2; \eta_2 + d\eta_2]$ and $[\zeta_2; \zeta_2 + d\zeta_2]$. Maxwell’s specification that those number were expressed in such a way “[o]n account of the mutual actions of the molecules” is quite misleading, because the interactions among the molecules have no place neither in that deduction nor in the

¹⁹ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 37.

search of the function $f(v)$ pursued in the following sections. Skipping Maxwell's further three-dimensional computation, we simply quote that "the number of encounters of the given kind between the two systems" should be proportional to $dN_1 dN_2$.²⁰

Then he devoted five pages to the procedures of integration with regard to the various parameters. In particular, the integration with regard the angle θ required the knowledge of the law of force acting between every couple of molecules. Having assumed a force proportional $1/r^n$, the expression to be integrated contained the term

$$V^{\frac{n-5}{n-1}}.$$

Experimental data on viscosity suggested $n=5$; from the mathematical point of view, this choice made easier the computation of the mentioned integral.²¹

In 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", Maxwell returned to the determination of the function of distribution for velocities. The title of the section is misleading once again, since no law of force was involved in the determination of the distribution. In the last passage of the preceding section he had reminded the reader about his previous paper (1860) on the same subject: he acknowledged that some assumptions there contained "may appear precarious" to him now. He would have determined "the form of the function in a different manner". He explicitly confined himself to distributions globally constant over time, wherein "the number of molecules whose velocity lies within given limits remains constant".²²

Among Maxwell's notes and drafts stored in "Cambridge University Library" there are few reference to the law of velocities distribution. In a manuscript which could be dated from 1862 to 1866, "On the Conduction of Heat in Gases", we read that he would have retained "the methods used in my former paper except when obliged to compare them with those of M. Clausius". Then he added that, if a great number of particles "are in motion in the same vessel", they cannot all have the same velocity, but "the average

²⁰ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 37-8.

²¹ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 40-1.

²² Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 43.

number of particles whose velocity lies within the limits v and $v+dv$ will follow the well-known law of errors

$$N \frac{4}{\alpha^3 \sqrt{\pi}} v^2 e^{-\frac{v^2}{\alpha^2}} dv \quad (1)$$

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 us that he was dealing with a mathematical model which, from the outset, was imagined as a statistical ensemble following the Gaussian law of errors.²³

In another manuscript, “Encounter of Two Molecules”, Maxwell insisted on “a step of philosophical importance” which “cannot be overestimated”; 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 tracing “the course of every molecule”, the latter is satisfied with “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 which are continuously exchanging molecules one with another”, entails the passage from “axioms absolutely certain” to “nothing more than a high probability”.²⁴ Here Maxwell did not specify what kind of uncertainty he was dealing with. In other words, does the uncertainty refer to an intrinsic lack of knowledge, or to the use of probabilistic algorithms, which are, in themselves, as “certain” as mechanical “axioms” or algorithms?

²³ *Maxwell Manuscript Collection*, Cambridge University Library; reproduced in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, pp. 339-40.

²⁴ *Maxwell Manuscript Collection*, Cambridge University Library; reproduced in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, p. 400.

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 focussed 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” 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 a 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”. The remaining part of the manuscript develops almost the same mechanical analysis then published in his 1867 paper.²⁵ 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 transformations, taking place at a different spatial scale, and ruled by the laws of statistics and probability.

If we return to the section of Maxwell’s 1867 paper devoted to the law of distribution of velocities, we see that he started, once again, from the collision between two particles, but then the mechanical analysis gives way to statistical and probabilistic remarks. If a and b are the velocities of two molecules of different kind before the collision, a' and b' are the velocities after the collision, and $f(v)$ is the required

²⁵ *Manuscript Collection*, Cambridge University Library; reproduced in Brush G., Garber E. and Everitt C.W.F. (eds.) 1986a, pp. 401-2.

distribution of velocities, then the number of molecules of the first kind endowed with the velocity a should be

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

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

$$n_2 = f_2(b) dV.^{26}$$

The key passage consists of two steps. First, Maxwell assumed that “the number of encounters of the given kind between these two sets of molecules” is 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' “is equal” to the number of couples (or collisions) wherein velocities are transformed from a' and b' into a and b . The first step corresponds to a hypothesis of independence between physical events: the members of a couple have no correlation. Molecules are looked upon as free particles: they have neither interactions nor history. This is quite strange from the point of view of physics: collisions are ruled by physical laws, and 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. The second step corresponds to a hypothesis of uniformity or equalisation over time: the fluctuations in the distribution of velocities are assumed to preserve the state of equilibrium. In some way, the equilibrium is 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,

²⁶ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 44.

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

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” ξ_1 and $\xi_1 + d\xi_1$, ... $[\xi_1; \xi_1 + d\xi_1]$, $[\eta_1; \eta_1 + d\eta_1]$ and $[\zeta_1; \zeta_1 + d\zeta_1]$ is

$$dN_1 = \frac{N_1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi d\eta d\zeta. \quad ^{27}$$

Maxwell felt obliged to specify that the above distribution was only “a possible form of the final distribution”. But, he added, it “is also the only form”; for another form, the exchange between a and a' “would not be equal”.²⁸ The statement does not appear so convincing from the logical point of view: the fact that one of the hypothesis, $f_1(a)f_2(b) = f_1(a')f_2(b')$, was necessary for the deduction of that distribution does not mean that another distribution should be incompatible with the hypothesis of the equal exchange between a and a' .

Even though Maxwell’s 1867 deduction of the law of distribution is really different from his 1860 deduction, it makes reference to the same probabilistic law: the product of probabilities for independent events. As already noticed, 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

²⁷ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 44-5.

²⁸ Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, p. 45.

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 better 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 as locally predictable and ruled by definite laws of motion, but globally unpredictable, even though leading to a distribution statistically uniform over time.²⁹

²⁹ It is worth remarking that 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.

2. *Swinging between discrete and continuous theoretical models*

In the 1870s, the Austrian physicists Ludwig Boltzmann tried to go far beyond Maxwell's microscopic interpretation of equilibrium in rarefied gases. At the time he held the chair of theoretical physics in Graz, and had already published some papers on different subjects. I will analyse only two fundamental papers he published in 1872 and 1877 in the *Wiener Berichte*: they represent two milestones in the history of Thermodynamics. Boltzmann theoretical pathway pursued a microscopic mechanical interpretation of the macroscopic features of a gas. As we will see, he managed to deepen and widen Maxwell approach: just like Maxwell, he did not manage to base his theory on purely mechanical hypotheses.¹

In the first lines of his 1872 paper, 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. The unpredictable motions he assume at the microscopic level gave rise to “well definite laws” at the macroscopic level, which involved those average values. The observable macroscopic processes were the result of unobservable microscopic events. Our limited perceptions allowed us to appreciate “no more than average values”, because of “the huge number of molecules in a body”, and their “swift motions”. Nevertheless, this subjective limitation did not represent an objective hindrance to a complete physical knowledge, for even “the most irregular processes” at the microscopic level led “to the same average values”.²

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. For every process, the ratio of the number of molecules whose properties “lie within a given range” to the total number of molecules had to be computed. Just at the end of the first page, Boltzmann sharply stated that “[p]roblems

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

² Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 316. The expression *Wiener Berichte* is usually used as a short form of “Sitzungsberichte der kaiserlichen Akademie der Wissenschaften – mathematisch-naturwissenschaftliche Classe”.

emerging from the mechanical theory of heat are probabilistic problems”. He was aware that the concept and the practice of probability echoed some kind of uncertainty and deficiency in natural knowledge. He was aware that the introduction of probability in physics raised both theoretical and meta-theoretical questions. In this case, probability was not a mere contingent tool, but had to be acknowledged as an intrinsic feature of the processes under investigation. 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 have confused an “incomplete demonstration” with a “completely demonstrated law of the theory of probability”.³ 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 notwendig 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.⁴

³ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 317-8.

⁴ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 316-7. With regard to the relationship between Boltzmann and what Cassirer called “Laplace’sche Geist” (title of the first chapter of Cassirer 1936 book), Cassirer himself emphasised that “objectivity (Gegenständlichkeit)” or objective “reality (Wirklichkeit)” did not require certainty or exact predictability but simply “legality (Gesetzlichkeit)”. (Cassirer E. 1936, p. 194) It seems to me that Cassirer managed to fully understand Boltzmann’s point of view. 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”. In some way, probability in the context of physics could not represent a problem in itself, provided that probability be ruled by some kind of

The 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”.⁵

Before undertaking the building up of the theory, Boltzmann listed other approximations and idealisations. He assumed that “every molecule spends most of its time flying with uniform rectilinear motion”. He 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” nor excluded “arbitrary forces” acting between the molecules. According to Boltzmann’s model, collisions among molecules attained three effects. Firstly, 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 velocities distribution, which was nothing else but the distribution of probability “for the different errors in the theory of least squares method”. He made explicitly reference to Maxwell’s theoretical researches: the number of molecules “whose velocities laid between v and $v+dv$ was represented by the function

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

mathematical law. Cassirer found that Boltzmann’s theory satisfied this requirement, and this makes us sure that we are dealing with a reliable physical theory.

⁵ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 317-8.

wherein A and B had constant values.⁶

According to Boltzmann, a question waited for a satisfactory answer: did every initial distribution of velocities tend towards Maxwell distribution over time? This was quite a demanding task, and he needed some other assumptions in order to undertake it. The walls of the vessel containing the gas reflected the molecules just like “elastic balls”. Every direction in space was equally probable for every molecule “after a very long time”. Indeed, a stronger assumption was immediately put forward: “from the outset, every direction was equally probable”. An even stronger one required that “the distribution of velocity was uniform at the beginning”.⁷

The most important 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. He was looking for a mathematical strategy suited to “a double-step 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.⁸ The keystone of the whole procedure was therefore the computation of the collisions. That a differential equation, namely a mathematical structure based on a continuous variation over time, depended on an intrinsically discontinuous process like a collision, sounds quite astonishing. Much more than the specific mathematical steps, this was the crucial challenge Boltzmann had to cope with. Moreover, the function $f(x,t)$ did not belong to the tradition of mathematical physics, even though it would have been processed by means of mathematical procedure belonging to the same tradition. In some way, a re-interpretation of the concepts of dynamic equation and evolution of a physical system was at stake. The function $f(x,t)$ represented a bridge between two different traditions of Mechanics: on the one hand, the laws of scattering between solid bodies, on the other the equations of motions. If the former dealt with discontinuous processes, the latter dealt with continuous ones. In the specific context of Boltzmann theory, the former was

⁶ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 318-9.

⁷ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 320-21.

⁸ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 322.

confined at the invisible, microscopic level of interacting molecules; the latter 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 Zusammenstoße 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

$$(1) \quad x + x' = \xi + \xi';$$

die Summe der lebendigen Kraft beider Moleküle vor dem Stoße ist gleich der Summe der lebendigen Kraft beider Moleküle nach demselben.⁹

A simple grid allowed Boltzmann to show the structure of the collision under consideration, wherein a is the first and b the second particle.

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

⁹ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 322-3.

This kind of collision strikes out a particle with living force lying between x and $x + dx$: as a consequence, the function $f(x,t) dx$ decreases by one. Boltzmann labelled dn the number of these collisions in the unitary volume in the time τ , and assumed that

$$(2) \quad dn = \tau \cdot f(x,t) dx f(x',t) \psi(x,x',\xi) dx' d\xi$$

$$(3) \quad \int dn = \tau \cdot dx \int_0^\infty \int_0^{x+x'} f(x,t) f(x',t) \psi(x,x',\xi) dx' d\xi,$$

wherein the function $\psi(x,x',t)$ “depends on the law of interaction” between a couple of particles.¹⁰

If some collisions destroy an amount of living force between x and $x + dx$, some others can create it. If the term $\int dn$ corresponded to a decrease of the function $f(x,t) dx$, there should be a term $\int dv$ corresponding to an increase of $f(x,t) dx$, in order that

$$(5) \quad f(x,t+d\tau) dx = f(x,t) dx - \int dn + \int dv.$$

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

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

and dv by the expression

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

¹⁰ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 323-4.

$$(11) \quad \int dv = \tau \cdot dx \int_0^{\infty} \int_0^{x+x'} f(\xi, t) f(x+x'-\xi, t) \psi(\xi, x+x'-\xi, x) dx' d\xi. ^{11}$$

Before inserting equations (3) and (11) into equation (5), Boltzmann developed the left-hand side of (5) in a series of Taylor:

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

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

This procedure allowed him to attain the 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 :

$$(12) \quad \frac{\partial f(x, t)}{\partial t} = \int_0^{\infty} \int_0^{x+x'} [f(\xi, t) f(x+x'-\xi, t) \psi(\xi, x+x'-\xi, x) - f(x, t) f(x', t) \psi(x, x', \xi)] dx' d\xi .^{12}$$

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

¹¹ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 326-7 and 331.

¹² Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 331-2.

$$(13) \quad \psi(x, x', \xi) = \psi(x', x, x + x' - \xi),$$

$$(14) \quad \sqrt{x x'} \psi(x, x', \xi) = \sqrt{\xi (x + x' - \xi)} \psi(\xi, x + x' - \xi, x).$$

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

$$(16) \quad \frac{\partial f(x, t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi, t)}{\sqrt{\xi}} \frac{f(x + x' - \xi, t)}{\sqrt{x + x' - \xi}} - \frac{f(x, t)}{\sqrt{x}} \frac{f(x', t)}{\sqrt{x'}} \right] \cdot \sqrt{x x'} \psi(x, x', \xi) dx' d\xi. \quad ^{13}$$

Immediately he remarked that the choice of the stationary function

$$(16a) \quad f(x, t) = f(x) = C \sqrt{x} e^{-hx},$$

wherein C and h were constant values, let $\partial f(x, t)/\partial t$ vanish in equation (16). Indeed, in this case,

$$\begin{aligned} \frac{\partial f(x, t)}{\partial t} &= \int_0^\infty \int_0^{x+x'} \left[\frac{C \sqrt{\xi} e^{-h\xi}}{\sqrt{\xi}} \frac{C \sqrt{x + x' - \xi} e^{-h(x + x' - \xi)}}{\sqrt{x + x' - \xi}} - \frac{C \sqrt{x} e^{-hx}}{\sqrt{x}} \frac{C \sqrt{x'} e^{-hx'}}{\sqrt{x'}} \right] \\ &\quad \cdot \sqrt{x x'} \psi(x, x', \xi) dx' d\xi = \\ &= \int_0^\infty \int_0^{x+x'} \left[e^{-h\xi} e^{-hx - hx' + h\xi} - e^{-hx} e^{-hx'} \right] \cdot \sqrt{x x'} \psi(x, x', \xi) dx' d\xi = 0 \end{aligned}$$

The fact is that the function (16a) was nothing else but Maxwell distribution of velocities, and the proof that $\partial f(x, t)/\partial t = 0$ was “nothing else but Maxwell’s demonstration translated into the present denotation”. In brief, the assumption of a Maxwellian distribution at a given time assured that such a distribution would not have

¹³ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 332-4.

changed over time. Boltzmann remarked that it was just “this and nothing else to have been demonstrated by Maxwell”.¹⁴

Boltzmann aimed at generalising Maxwell’s outcome: starting from “an arbitrary distribution of living force”, he wondered “how does it change over time”. We expect he should have tried to solve equation (16), but he undertook an apparent detour, for he focussed on another function generated by $f(x,t)$,

$$(17) \quad E = \int_0^{\infty} f(x,t) \left\{ \log \left[\frac{f(x,t)}{\sqrt{x}} - 1 \right] \right\} dx.$$

He rather tried to prove that E “could not increase, provided that the function $f(x,t)$... satisfies equation (16)”. He then began a long and demanding computation, which involved some transformations of the new integral

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

Before undertaking the transformations, Boltzmann put the expression for $\partial f(x,t)/\partial t$ inside the last integral:

$$\begin{aligned} \frac{dE}{dt} &= \int_0^{\infty} \log \left(\frac{f(x,t)}{\sqrt{x}} \right) dx \cdot \int_0^{\infty} \int_0^{x+x'} \left[\frac{f(\xi,t)}{\sqrt{\xi}} \frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}} - \frac{f(x,t)}{\sqrt{x}} \frac{f(x',t)}{\sqrt{x'}} \right] \\ &\quad \cdot \sqrt{x x'} \psi(x, x', \xi) dx' d\xi = \\ (18) \quad &= \int_0^{\infty} \int_0^{\infty} \int_0^{x+x'} \left[\frac{f(\xi,t)}{\sqrt{\xi}} \frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}} - \frac{f(x,t)}{\sqrt{x}} \frac{f(x',t)}{\sqrt{x'}} \right] \cdot \log \left(\frac{f(x,t)}{\sqrt{x}} \right) \\ &\quad \cdot \sqrt{x x'} \psi(x, x', \xi) dx dx' d\xi \end{aligned} \quad .^{15}$$

¹⁴ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 334.

¹⁵ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 335.

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 the 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

$$\begin{aligned} \frac{dE}{dt} &= \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot \log(s) \cdot r \cdot dx dx' d\xi, \\ \frac{dE}{dt} &= \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot \log(s') \cdot r \cdot dx dx' d\xi, \\ \frac{dE}{dt} &= - \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot \log(\sigma) \cdot r \cdot dx dx' d\xi, \\ \frac{dE}{dt} &= - \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot \log(\sigma') \cdot r \cdot dx dx' d\xi. \end{aligned} \quad ^{16}$$

The equality of the four integrals let Boltzmann write

$$\begin{aligned} \frac{dE}{dt} &= \frac{1}{4} \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot [\log(s) + \log(s') - \log(\sigma) - \log(\sigma')] \cdot r \cdot dx dx' d\xi \\ (24) \quad &= \frac{1}{4} \int_0^\infty \int_0^\infty \int_0^{x+x'} (\sigma \sigma' - s s') \cdot \log\left(\frac{s \cdot s'}{\sigma \cdot \sigma'}\right) \cdot r \cdot dx dx' d\xi \end{aligned}$$

¹⁶ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 343-4.

This was the end of the computation: the solution of Boltzmann problem consisted in drawing a simple algebraic conclusion about the expression

$$(\sigma\sigma' - s s') \cdot \log\left(\frac{s \cdot s'}{\sigma \cdot \sigma'}\right).$$

If $\sigma\sigma' > s s'$, then $\log\left(\frac{s \cdot s'}{\sigma \cdot \sigma'}\right) < 0$; if $\sigma\sigma' < s s'$, then $\log\left(\frac{s \cdot s'}{\sigma \cdot \sigma'}\right) > 0$. In any case, the above expression is negative, and “the whole integral is necessarily negative”. This means that “ E must necessarily decrease”. For Boltzmann excluded that “ E could become infinitely negative”, he expected that it approached a minimum value, wherein $dE/dt = 0$. In this specific case, $\sigma\sigma' = s s'$ (25), namely

$$\frac{f(\xi, t)}{\sqrt{\xi}} \frac{f(x + x' - \xi, t)}{\sqrt{x + x' - \xi}} = \frac{f(x, t)}{\sqrt{x}} \frac{f(x', t)}{\sqrt{x'}}.$$

The condition $dE/dt = 0$ corresponded to $df/dt = 0$, and it was satisfied for every stationary function of the kind

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

If we accept Boltzmann assumption that the evolution of the physical system led to $dE/dt = 0$, we must accept that the system approaches Maxwell distribution of velocities.¹⁷

The fact is that the mathematical proof assures us that the condition is sufficient, but not necessary. Nevertheless, 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”. The

¹⁷ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 344-5.

statement had an even deeper physical meaning, for it could be interpreted as “an analytic proof of the second principle” of Thermodynamics. He thought to have attained the proof of the second Principle “through a completely different pathway”. The quantity dE/dt could be associated to the integral $\int dQ/T$: what had been demonstrated about dE/dt could be translated into a statement about $\int dQ/T$. 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 theoretical method was more general in its nature, for it did not find difficult to cope with irreversible processes. Indeed, irreversible processes were the ones “really taking place in nature”, whereas the reversible ones were “purely ideal”.¹⁸

In the next section of the essay, the complex interplay between mathematical algorithms and physical concepts was newly on the stage, for Boltzmann faced the opposition between continuous and discrete models. The physical side of the opposition involved the comparison between continuous and discrete models of matter. The mathematical side involved, in particular, the comparison between integrals and infinite sums. According to the foundations of the integral-differential calculus,

$$\begin{aligned} \int_0^{\infty} f(x,t)dx &= \lim_{\varepsilon \rightarrow 0; p \rightarrow \infty} \sum_{p=1}^{\infty} \varepsilon \cdot f(p\varepsilon, t) = \\ &= \lim_{\varepsilon \rightarrow 0; p \rightarrow \infty} \sum_{p=1}^{\infty} \varepsilon \cdot [f(\varepsilon, t) + f(2\varepsilon, t) + \dots + f(p\varepsilon, t) + \dots] \end{aligned}$$

It is easy to imagine that, in the physical context, Boltzmann preferred the discrete model, in accordance with the foundations of the kinetic theory of gases. It is more difficult to imagine that a physicist trained in the tradition of mathematical physics would have liked to replace integrals with infinite sum, but this was just what Boltzmann did.¹⁹ We cannot say that there was some kind of contradiction: indeed,

¹⁸ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 345-6.

¹⁹ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 346.

discrete mathematical methods suited physical discrete models more than continuous ones. It is worth quoting some Boltzmann passages.

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.²⁰

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 of a given amount ε . This is perhaps the most astonishing feature of Boltzmann new theoretical model: energy, just like matter, had to rely on a basic unit. In other words, Boltzmann put forward an atomic or molecular representation of energy besides an atomic or molecular representation of matter. 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 conservation of energy required that

$$(27) \quad k + l = \chi + \lambda. \quad ^{21}$$

In Boltzmann 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

²⁰ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 347.

²¹ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 348-9.

$$(28) \quad N_{\chi\lambda}^{kl} = \tau \cdot w_k \cdot w_l \cdot A_{\chi\lambda}^{kl}.$$

The above equation was the discrete analogous of the equation (2), which defined the continuous function dn . The functions $A_{\chi\lambda}^{kl}$ was the discrete analogous of the continuous function $\psi(x, x', t)$. The discrete analogous of the symmetries expressed by equation (14) led Boltzmann to define a new function $B_{\chi\lambda}^{kl} = \sqrt{kl} A_{\chi\lambda}^{kl}$, which transformed equation (28) into

$$(32) \quad N_{\chi\lambda}^{kl} = \tau \cdot \frac{w_k w_l}{\sqrt{kl}} \cdot B_{\chi\lambda}^{kl}.$$

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

$$(31) \quad B_{\chi\lambda}^{kl} = B_{kl}^{\chi\lambda}.^{22}$$

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 collision destroying the energy ε :

$$(33) \quad w_1' = w_1 - N_{22}^{13} - N_{23}^{14} - N_{32}^{14} - N_{24}^{15} + \dots + N_{13}^{22} + N_{14}^{23} + N_{14}^{32} + N_{15}^{24} + \dots.$$

Another Taylor development allowed Boltzmann to write

²² Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 349-50.

$$w_1' = w_1 + \tau \frac{dw_1}{dt},$$

$$\begin{aligned} \frac{dw_1}{dt} = & -\frac{w_1 w_3}{\sqrt{1 \cdot 3}} \cdot B_{22}^{13} - \frac{w_1 w_4}{\sqrt{1 \cdot 4}} \cdot B_{23}^{14} - \frac{w_1 w_4}{\sqrt{1 \cdot 4}} \cdot B_{32}^{14} - \frac{w_1 w_5}{\sqrt{1 \cdot 5}} \cdot B_{24}^{15} - \dots \\ & + \frac{w_2 w_2}{\sqrt{2 \cdot 2}} \cdot B_{13}^{22} + \frac{w_2 w_3}{\sqrt{2 \cdot 3}} \cdot B_{14}^{23} + \frac{w_3 w_2}{\sqrt{3 \cdot 2}} \cdot B_{14}^{32} + \frac{w_2 w_4}{\sqrt{2 \cdot 4}} \cdot B_{15}^{24} + \dots \end{aligned}$$

A transformation on the couple of weights w_k and w_l , which was nothing else but the reverse of the transformation on $A_{\chi\lambda}^{kl}$, led Boltzmann to define the new weights

$$u_k = \frac{w_k}{\sqrt{k}}$$

and the new equations

$$\begin{aligned} \frac{du_1}{dt} = & -u_1 u_3 \cdot B_{22}^{13} - u_1 u_4 \cdot B_{23}^{14} - u_1 u_4 \cdot B_{32}^{14} - u_1 u_5 \cdot B_{24}^{15} - \dots \\ & + u_2 u_2 \cdot B_{13}^{22} + u_2 u_3 \cdot B_{14}^{23} + u_3 u_2 \cdot B_{14}^{32} + u_2 u_4 \cdot B_{15}^{24} + \dots \end{aligned}$$

The complete system of equations was therefore

$$\begin{aligned} \frac{du_1}{dt} &= (u_2^2 - u_1 u_3) \cdot B_{22}^{13} + (u_2 u_3 - u_1 u_4) \cdot (B_{23}^{14} + B_{32}^{14}) + \dots \\ (35) \quad \sqrt{2} \frac{du_2}{dt} &= 2(u_1 u_3 - u_2^2) \cdot B_{22}^{13} + (u_1 u_4 - u_2 u_3) \cdot (B_{23}^{14} + B_{32}^{14}) + \dots \\ &\dots \dots \\ \sqrt{p} \frac{du_p}{dt} &= (u_2 u_{p-1} - u_1 u_p) \cdot (B_{2,p-1}^{1,p} + B_{p-1,2}^{1,p}) + \dots \end{aligned}$$

²³ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 351-2.

If we compare equation (35), which stemmed from a discrete model, with equation (16), which stemmed from a continuous model, we found a system of p ordinary differential equations instead of a single complex integral-differential equation.²⁴

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

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

and its time derivative

$$\begin{aligned} \frac{dE}{dt} &= \left[\frac{du_1}{dt} \cdot \log(u_1) + u_1 \frac{1}{u_1} \frac{du_1}{dt} \right] + \sqrt{2} \left[\frac{du_2}{dt} \cdot \log(u_2) + u_2 \frac{1}{u_2} \frac{du_2}{dt} \right] + \\ &\quad + \sqrt{3} \left[\frac{du_3}{dt} \cdot \log(u_3) + u_3 \frac{1}{u_3} \frac{du_3}{dt} \right] + \dots + \sqrt{p} \left[\frac{du_p}{dt} \cdot \log(u_p) + u_p \frac{1}{u_p} \frac{du_p}{dt} \right], \\ \frac{dE}{dt} &= \frac{du_1}{dt} \cdot \log(u_1) + \sqrt{2} \frac{du_2}{dt} \cdot \log(u_2) + \sqrt{3} \frac{du_3}{dt} \cdot \log(u_3) + \dots + \sqrt{p} \frac{du_p}{dt} \cdot \log(u_p) \\ &\quad + \frac{du_1}{dt} + \sqrt{2} \frac{du_2}{dt} + \sqrt{3} \frac{du_3}{dt} + \dots + \sqrt{p} \frac{du_p}{dt}. \end{aligned}$$

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 is not modified by this simplification. If

$$\begin{aligned} \frac{du_1}{dt} &= (u_2^2 - u_1 u_3) \cdot B_{22}^{13} \\ (36) \quad \sqrt{2} \frac{du_2}{dt} &= 2(u_1 u_3 - u_2^2) \cdot B_{22}^{13}, \\ \sqrt{3} \frac{du_3}{dt} &= (u_2^2 - u_1 u_3) \cdot B_{22}^{13} \end{aligned}$$

then

²⁴ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 353.

$$\frac{dE}{dt} = (u_2^2 - u_1 u_3) \cdot B_{22}^{13} \cdot [\log(u_1) - 2\log(u_2) + \log(u_3)] \quad .^{25}$$

This is the crucial step of Boltzmann demonstration in the discrete model. The structure of the equation

$$\frac{dE}{dt} = B_{22}^{13} \cdot (u_2^2 - u_1 u_3) \cdot \log\left(\frac{u_1 u_3}{u_2^2}\right)$$

is not so different from the equation (24), which stemmed from a continuous model. He could therefore repeat those algebraic remarks. In the above equation, 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 $dE/dt = 0$. In conclusion, the function E is decreasing, and it “approaches its minimum value”.²⁶

After having faced the case of polyatomic molecules, at the end of his 1872 paper, Boltzmann came back to the relationship between the function E and the entropy. For bodies “whose atoms have realised the thermal equilibrium”, he defined the function

$$(94) \quad E^* = N \iint f^* \log(f^*) ds d\sigma,$$

wherein N was “the number of the gas molecules”, $f^* = f/N$, $d\sigma = dx_1 dy_1 dz_1 dx_2 \dots dx_r dy_r dz_r$ the hyper-volume of integration over space, and $ds = du_1 dyv dw_1 du_2 \dots du_r dv_r dw_r$ the hyper-volume of integration over velocities.

For a mono-atomic gas,

²⁵ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 354.

²⁶ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 355.

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

wherein 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

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

As Boltzmann remarked, the above expression “corresponds to the entropy of a mono-atomic gas, apart from a constant factor and addend”.²⁷

At the end, two important features of Boltzmann computation deserve to be emphasised. First, Boltzmann forced the laws of mechanics and the laws of probability 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. In some way, the whole could not be considered as a mere sum of its microscopic parts.²⁸

The apparent contradiction between the reversibility of individual collisions and the irreversibility of the global evolution, which stemmed from the hypothesis of dynamical independence of the molecules, raised some debate. Some physicists began to wonder what should have happened in case we had managed to instantaneously reverse the velocity of every molecule. Could the system go upstream, and therefore away from the equilibrium? Apart from the huge amount of energy and information required in order

²⁷ Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 399-400.

²⁸ 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.”

to perform the hypothetical inversion, the fact is that collisions among dynamically independent molecules cannot lead the system backwards.²⁹

²⁹ With regard to criticism about Boltzmann theory, in particular Loschmidt criticism, see Dugas R. 1959, pp. 160 and 180. Se also Brush S. 1976, book 1, p. 239.

3. From mechanical models to probability

In the long paper Boltzmann published in 1877, he reminded the reader that the function E he had introduced in his 1872 paper could never increase, and that it reached its minimum value at the thermal equilibrium. He also reminded the reader about a recently published paper, “Bemerkungen über einige Probleme der mechanischen Wärmetheorie”, wherein he had stated that “there are more uniform than non-uniform distributions” of living force among the molecules of a gas; as a consequence, a “greater probability that the distribution become uniform over time” followed.¹

Indeed, the relationship between the second Principle of Thermodynamics and the probability of the distributions of the energy was the theoretical issue underlying Boltzmann 1877 paper. In the second page, he put forward four hypotheses. First, in most cases “the initial state was an improbable one”: in other words, in the course of some transformation, the gas can be found in a state far from the equilibrium. 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. Four, 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 mögliche Zustände des Systems aufsucht. Der Anfangszustand 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 dem Wahrscheinlichkeit des betreffenden Zustandes identifizieren.²

¹ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 164.

² Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 165.

As in his 1872 paper, Boltzmann did not like to confine himself to the states of equilibrium: here, in particular, he tried to compute the probability of all possible “distributions of state”. His physical model of gas was not so far from the model he had put forward seven 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 are less than a given value”, they were allowed to interact. This peculiar, unnatural model of force, defined by a sharp discontinuity in its mathematical law, allowed Boltzmann to pursue two targets. On the one hand, he tried to derive similar effects by two different causes, stemming from two different mechanical traditions: intrinsically discontinuous collisions or intrinsically continuous forces. On the other hand, he tried to combine two subsequent steps in molecular processes: the continuity of the unperturbed trajectories, and the discontinuity of sudden collisions.³

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” with an upper bound $P = p\varepsilon$:

$$0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots, p\varepsilon.$$

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

$$\lambda \cdot \varepsilon = L.^4$$

³ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 166. Dugas reminded us that Boltzmann theoretical representation of atoms and molecules evolved over time. In his *Vorlesungen über Gastheorie* (1895-1898), in the first volume 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.

⁴ 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 are many complexions corresponding to the state. Boltzmann labelled $\mathfrak{B}$ “the number of complexions” or “number of permutations” or “permutability of a given distribution”. The discrete *function* $\mathfrak{B}$ played in the 1877 essay the crucial role played by the discrete *function* $N_{\chi\lambda}^{kl}$ in the 1872 paper.⁵

In order to better explain the meaning of $\mathfrak{B}$, Boltzmann offered a “simple numerical instance” wherein $n = 7$, $\lambda = 7$, $p = 7$, and therefore $L = 7\varepsilon$ and $P = 7\varepsilon$. He showed that, in this case, there were 15 possible states: to each of them corresponded a precise number of internal permutations.

	state	$\mathfrak{B}$				state	$\mathfrak{B}$
1	0000007	7			9	0001114	140
2	0000016	42			10	0001123	420
3	0000025	42			11	0001222	140
4	0000034	42			12	0011113	105
5	0000115	105			13	0011122	210
6	0000124	210			14	0111112	42
7	0000133	105			15	1111111	1
8	0000223	105					

In the computation, Boltzmann assumed that we could distinguish the molecules from each other. In the table above, in the first state, one molecule owns the energy 7ε , and the others zero energy: in the complexion showed in the corresponding cell, the first six

⁵ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 169-70.

molecules own zero energy and the last 7ε energy. There are other complexions corresponding to the same state: the complexion wherein the first molecule owns 7ε energy and the others zero, the complexion wherein the second owns 7ε and the others zero, and so on. The number of complexions corresponding to the state wherein only one molecule owns 7ε and the other zero is 7, as showed in the corresponding cell.

Die erste Zustandsverteilung z. B. ist dadurch charakterisiert, daß 6 Molekülen die lebendige Kraft Null, einem die lebendige Kraft 7ε zukommt, d.h., daß $w_0=6$, $w_7=1$, $[w_1=]w_2=w_3=w_4=w_5=w_6=0$ ist. Welches der Moleküle die lebendige Kraft 7ε hat, ist dabei gleichgültig. Alle möglichen Komplexionen, welche dieser Zustandsverteilung entsprechen, sind daher 7 an der Zahl. Bezeichnen wir die Gesamtzahl aller Komplexionen, also in unserem Falle die Zahl 1716 durch J, so ist also die Wahrscheinlichkeit der ersten Zustandsverteilung $7/J$; ebenso ist die Wahrscheinlichkeit der zweiten Zustandsverteilung $42/J$; am größten ist die Wahrscheinlichkeit der zehnten Zustandsverteilung, da sich ihre Elemente am öftesten permutieren lassen.⁶

The computation of the “permutability” $\mathfrak{B}$ was submitted to the conservation of matter and energy:

$$(1) \quad w_0 + w_1 + w_2 + \dots + w_p = n$$

$$(2) \quad 0w_0 + 1w_1 + 2w_2 + \dots + pw_p = \lambda$$

The table above displayed was consistent with the choice

$$(3) \quad \mathfrak{B} = \frac{n!}{(w_0)! \cdot (w_1)! \cdot (w_2)! \cdot \dots \cdot (w_p)!}.$$

⁶ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 170-1.

For every state, the number of complexions was the number of permutation of all the molecules divided by the number of internal permutations of every set of molecules owning the same energy. We can notice 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 $\mathfrak{B}$ a great number, whereas a very symmetric distribution makes the denominator much lesser. This means that the number of complexions $\mathfrak{B}$ is little for asymmetric distributions of energy, and is great for symmetric distributions.⁷ The computation is quite easy in the two limiting cases: a single $w_k = n$, which means an extremely asymmetric distribution, and $w_k = n/p$ for every k , which means a uniform or symmetric distribution of energies. In the first case,

$$\mathfrak{B} = \frac{n!}{(0)! \cdot (0)! \cdot \dots \cdot (n)! \cdot \dots \cdot (0)!} = 1.$$

In the second case,

$$\mathfrak{B} = \frac{n!}{(n/p)! \cdot (n/p)! \cdot (n/p)! \cdot \dots \cdot (n/p)!} = \frac{n!}{p \cdot (n/p)!}$$

If n and p are supposed to be very great numbers, as in the case of a real gas, or equal numbers as Boltzmann had assumed in the above table,

$$\mathfrak{B} = \frac{n!}{p \cdot (n/p)!} = \frac{n!}{n \cdot (1)!} = (n-1)!,$$

which would be an extremely great number for a real gas. In brief, Boltzmann mathematical law for the computation of the complexions entailed a great number of complexions for symmetric or uniform distributions of energy, and a little number of complexions for an asymmetric or non-uniform distribution of energy.

⁷ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 175-6.

After this semi-qualitative analysis, let me return to Boltzmann search for the exact mathematic determination of “the most probable distribution of state”. He first stated that the maximum of $\mathfrak{B}$ was the minimum of its denominator, because the numerator “is constant” in any case. Then he noticed that the minimum of the denominator was the minimum of its logarithm, because the denominator “is a product” of factorials. The expression to minimise was therefore

$$(4) \quad \begin{aligned} M &= \ln[(w_0)! \cdot (w_1)! \cdot (w_2)! \cdot \dots \cdot (w_p)!] \\ &= \ln[(w_0)!] + \ln[(w_1)!] + \ln[(w_2)!] + \dots + \ln[(w_p)!] \end{aligned}$$

At this point, he suddenly changed his model, “in order to apply the differential calculus” to a computation based on the discrete structure of the integer numbers. He transformed the factorial function into the Gamma function, which was a generalisation of the factorial function, extended to continuous numerical sets. If

$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x} dx,$$

we can show that

$$\Gamma(n) = (n-1)! \quad \text{or} \quad \Gamma(n+1) = (n)!.$$

According to this generalisation, equation (4) was translated into

$$(4a) \quad M_1 = \ln[\Gamma(w_0 + 1)] + \ln[\Gamma(w_1 + 1)] + \ln[\Gamma(w_2 + 1)] + \dots + \ln[\Gamma(w_p + 1)].^8$$

⁸ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 176. In the 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 imagine 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

The search for the minimum of M_1 was performed by Boltzmann with the help of the procedure of Lagrange multipliers. For a given function $f(w_0, w_1, w_2, \dots, w_p)$ to be minimized under a set of conditions $g_k(w_0, w_1, w_2, \dots, w_p) = 0$, the problem of minimization can be carried on by the help of the stationary points of Lagrange function

$$\Lambda(w_0, w_1, w_2, \dots, w_p; h_1, h_2, \dots, h_\lambda) = f(w_0, w_1, w_2, \dots, w_p) + \sum_{k=1}^{\lambda} h_k \cdot g_k(w_0, w_1, w_2, \dots, w_p).$$

The set of numbers or *multipliers* h_k can be found at the end of the procedure. In the specific problem Boltzmann was facing, the function M_1 was submitted to condition (1) and (2): therefore

$$\begin{aligned} \Lambda(w_0, w_1, w_2, \dots, w_p; h, k) &= \\ &= \ln[\Gamma(w_0 + 1)] + \ln[\Gamma(w_1 + 1)] + \ln[\Gamma(w_2 + 1)] + \dots + \ln[\Gamma(w_p + 1)] + h \cdot n + k \cdot \lambda \end{aligned}$$

The partial derivatives of the function $\Lambda(w_0, w_1, w_2, \dots, w_p; h, k)$ must vanish:

$$\begin{aligned} \frac{\partial \ln[\Gamma(w_0 + 1)]}{\partial w_0} + h &= 0, \\ \frac{\partial \ln[\Gamma(w_1 + 1)]}{\partial w_1} + h + k &= 0, \\ \frac{\partial \ln[\Gamma(w_2 + 1)]}{\partial w_2} + h + 2k &= 0, \\ &\dots \dots \dots \\ \frac{\partial \ln[\Gamma(w_p + 1)]}{\partial w_p} + h + pk &= 0. \end{aligned}$$

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 approach to that conceptual tension, see Dugas R. 1959, p. 73.

In the series of the last equations, the differences between two subsequent derivatives is always k ; this means that

$$(5) \quad \frac{\frac{\partial \ln[\Gamma(w_1+1)]}{\partial w_1} - \frac{\partial \ln[\Gamma(w_0+1)]}{\partial w_0}}{\frac{\partial \ln[\Gamma(w_3+1)]}{\partial w_3} - \frac{\partial \ln[\Gamma(w_2+1)]}{\partial w_2}} = \frac{\frac{\partial \ln[\Gamma(w_2+1)]}{\partial w_2} - \frac{\partial \ln[\Gamma(w_1+1)]}{\partial w_1}}{\dots\dots\dots} = \dots\dots\dots^9$$

Another mathematical switch took place at this point, for Boltzmann re-translated the expression M into a discrete form, making use of the approximation

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

The terms $\frac{\partial \ln[\Gamma(w_k+1)]}{\partial w_k} - \frac{\partial \ln[\Gamma(w_{k-1}+1)]}{\partial w_{k-1}}$ were therefore translated into

$$\frac{\partial \left[\ln \left(\frac{w_k}{e} \right)^{w_k} \right]}{\partial w_k} - \frac{\partial \left[\ln \left(\frac{w_{k-1}}{e} \right)^{w_{k-1}} \right]}{\partial w_{k-1}} = \frac{\partial \left[w_k \cdot \ln \left(\frac{w_k}{e} \right) \right]}{\partial w_k} - \frac{\partial \left[w_{k-1} \cdot \ln \left(\frac{w_{k-1}}{e} \right) \right]}{\partial w_{k-1}} =$$

$$\ln \left(\frac{w_k}{e} \right) + w_k \frac{e}{w_k} \frac{1}{e} - \ln \left(\frac{w_{k-1}}{e} \right) - w_{k-1} \frac{e}{w_{k-1}} \frac{1}{e} =$$

$$\ln \left(\frac{w_k}{e} \right) + 1 - \ln \left(\frac{w_{k-1}}{e} \right) - 1 = \ln \left(\frac{w_k}{e} \right) - \ln \left(\frac{w_{k-1}}{e} \right) =$$

$$\ln w_k - \ln e - \ln w_{k-1} + \ln e = \ln w_k - \ln w_{k-1}.$$

The set of equations (5) became

$$\ln w_1 - \ln w_0 = \ln w_2 - \ln w_1 = \ln w_3 - \ln w_2 = \dots\dots\dots$$

⁹ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 177. From the mathematical point of view, the procedure yields only a necessary condition.

and therefore

$$(6c) \quad \frac{w_1}{w_0} = \frac{w_2}{w_1} = \frac{w_3}{w_2} = \dots\dots\dots,$$

because of the known properties of logarithms. This means that

$$(7) \quad w_1 = x \cdot w_0; \quad w_2 = x \cdot w_1 = x^2 \cdot w_0; \quad w_3 = x^3 \cdot w_0; \quad \dots\dots\dots^{10}$$

The fundamental laws of conservation (1) and (2) could be written as functions of x :

$$(1) \quad w_0(1 + x + x^2 + \dots\dots + x^p) = n$$

$$(2) \quad w_0(x + 2x^2 + 3x^3 + \dots\dots + px^p) = \lambda.$$

The system contains the two variables x and w_0 : Boltzmann managed to derive an equation containing only x , discussed the features of the solutions, and tried to solve the equation numerically in specific cases. This part of the paper is not of particular interest for us, because no general solution is attained.¹¹

More interesting is the subsequent section, wherein Boltzmann tried to develop a more consistent continuous model for the distribution of energy. The quantity ε was interpreted as “a very small quantity”, and the frequencies $w_0, w_1, w_2, \dots\dots w_p$ were expressed by means of a continuous function $f(x)$:

$$(19) \quad w_0 = \varepsilon \cdot f(0); \quad w_1 = \varepsilon \cdot f(\varepsilon); \quad w_2 = \varepsilon \cdot f(2\varepsilon); \quad \dots\dots\dots$$

¹⁰ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 178.

¹¹ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 178-85.

Nevertheless he still relied on the expression for the number of distributions, which stemmed by the first discrete model,

$$\mathfrak{B} = \frac{n!}{(w_0)! \cdot (w_1)! \cdot (w_2)! \cdot \dots \cdot (w_p)!},$$

and on the approximation $w_k! = \sqrt{2\pi} (w_k/e)^{w_k}$. In this case, the expression to be minimised was the already known denominator

$$\begin{aligned} M &= \ln \left[\left(\frac{w_0}{e}\right)^{w_0} \cdot \left(\frac{w_1}{e}\right)^{w_1} \cdot \left(\frac{w_2}{e}\right)^{w_2} \cdot \dots \cdot \left(\frac{w_p}{e}\right)^{w_p} \right] \\ &= \ln \left(\frac{w_0}{e}\right)^{w_0} + \ln \left(\frac{w_1}{e}\right)^{w_1} + \ln \left(\frac{w_2}{e}\right)^{w_2} + \dots + \ln \left(\frac{w_p}{e}\right)^{w_p} \\ &= w_0 (\ln w_0 - \ln e) + w_1 (\ln w_1 - \ln e) + w_2 (\ln w_2 - \ln e) + \dots + w_p (\ln w_p - \ln e) \\ &= w_0 \ln w_0 + w_1 \ln w_1 + w_2 \ln w_2 + \dots + w_p \ln w_p - (w_0 + w_1 + w_2 + \dots + w_p).^{12} \\ &= w_0 \ln w_0 + w_1 \ln w_1 + w_2 \ln w_2 + \dots + w_p \ln w_p - n \end{aligned}$$

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:

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

¹² Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 187-8.

and in the fundamental laws of conservation

$$(1) \quad \varepsilon[f(0) + f(\varepsilon) + f(2\varepsilon) + \dots + f(p\varepsilon)] = n$$

$$(2) \quad \varepsilon[0 \cdot f(0) + \varepsilon \cdot f(\varepsilon) + 2\varepsilon \cdot f(2\varepsilon) + \dots + p\varepsilon \cdot f(p\varepsilon)] = L.$$

Boltzmann neglected the term containing only n and ε , for “they are constant”: in particular, ε “has the same value for all the distributions of state”. The expression M to be minimized could be replaced by

$$(24) \quad M' = \varepsilon[f(0) \ln f(0) + f(\varepsilon) \ln f(\varepsilon) + f(2\varepsilon) \ln f(2\varepsilon) + \dots + f(p\varepsilon) \ln f(p\varepsilon)].^{13}$$

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

$$(25) \quad M' = \int_0^\infty f(x) \ln[f(x)] dx$$

$$(26) \quad n = \int_0^\infty f(x) dx$$

$$(27) \quad L = \int_0^\infty x \cdot f(x) dx.^{14}$$

The procedure of Lagrange multipliers was on the stage once again, in order to minimize the expression (25) under the conditions (26) and (27). The search for stationary points was performed on the integral

$$\int_0^\infty \{f(x) \ln[f(x)] + kf(x) + hxf(x)\} dx,$$

¹³ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 188.

¹⁴ Boltzmann L. 1877, in Boltzmann L. 1909, II Band, p. 188.

whose variation is

$$\int_0^{\infty} \left\{ f'(x) \ln[f(x)] + f(x) \frac{f'(x)}{f(x)} + kf'(x) + hf'(x) + hxf'(x) \right\} dx =$$

$$\int_0^{\infty} \left\{ \ln[f(x)] + 1 + k + h + kx \right\} f'(x) dx$$

The variation vanishes when $\ln[f(x)] + 1 + k + h + hx = 0$ or $\ln[f(x)] = -1 - k - h - hx$. The solution is

$$(28) \quad f(x) = e^{-1-k-h-hx} = e^{-1-k-h} e^{-hx} = C e^{-hx}.$$

This function was interpreted by Boltzmann in the usual way: it “would yield the result that, at the thermal equilibrium, the probability of a living force lying between x and $x+dx$ ” is

$$f(x) dx = C e^{-hx} dx.^{15}$$

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

$$(61) \quad \Omega = - \iiint \iiint f(x,y,z;u,v,w) \ln[f(x,y,z;u,v,w)] dx dy dz du dv dw ,$$

wherein 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

¹⁵ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 189-90. Boltzmann showed that “the second variation of M ” was necessarily positive, and therefore the function (28) represented really a minimum.

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 showed, at the equilibrium,

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

wherein 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

$$(62) \quad \Omega = N \log \left[V \left(\frac{4\pi T}{3m} \right)^{3/2} \right] + \frac{3}{2} N - N \ln N.^{16}$$

In general, from a purely mathematical point of view, the above expression could be written as

$$\Omega = N \ln(VT^{3/2}) + K,$$

where K is a constant term, independent of the variables V and T .

Apart from the reversed signs and the last constant in the right-hand side of (62), Boltzmann arrived essentially at the expression already found in 1872. At that time, he briefly stated that it corresponded essentially to “the entropy of a mono-atomic gas”. Seven 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:

¹⁶ 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 by D. EnsKog and S. Chapman in 1916-7. See Brush 1976, book 1, p. 237, and Brush 1976, book 2, p. 449.

$$(63) \quad dQ = NdT + pdV$$

$$(64) \quad pV = \frac{2}{3}NT.$$

The computation of entropy required only a simple integration:

$$\begin{aligned} \int \frac{dQ}{T} &= \int N \frac{dT}{T} + \int \frac{pdV}{T} = N \ln T + C_1 + \int \frac{2}{3} \frac{NT}{VT} dV = N \ln T + C_1 + \frac{2}{3} N \int \frac{dV}{V} \\ &= N \ln T + C_1 + \frac{2}{3} N \ln V + C_2 = \frac{2}{3} N \left(\frac{3}{2} \ln T + \ln V \right) + C = \frac{2}{3} N \left(\frac{3}{2} \ln T^{3/2} + \ln V \right) + C \\ &= \frac{2}{3} N \ln(VT^{3/2}) + C.^{17} \end{aligned}$$

Boltzmann stressed the structural similarity between the function Ω , representing the probability of a given state, and the entropy dQ/T , in whatever “reversible change of state”. Apart from a constant,

$$\int \frac{dQ}{T} = \frac{2}{3} \Omega :$$

the increase of “the measure of permutability multiplied by $2/3$ ” equals “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

¹⁷ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, p. 216. For a comparison, see Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 399-400.

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 den Entropie identisch ist, welche aber auch während des Verlaufes eines nicht umkehrbaren Körpers einen Sinn behält, und auch während eines solchen fortwährend zunimmt.¹⁸

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 measure of permutability of all bodies in the course of the transformation “*will continuously increase*”, or at most “*can maintain a constant value as long as all the bodies are in thermal equilibrium*”.

At the end, in the last passages, 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”.¹⁹

Boltzmann was aware of the originality of his contribution to Thermodynamics; at the same time, he was aware that his mathematical model represented a simplification and an idealisation. What he did not explicitly wondered was whether he had actually

¹⁸ 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”.

¹⁹ Boltzmann L. 1877b, in Boltzmann L. 1909, II Band, pp. 217-8 and 233.

managed or not to give a mechanical explanation of the second Principle of Thermodynamics. In some way, he let people believe he had managed, and this belief triggered off the subsequent widespread debate on the possibility or impossibility of a mechanical foundation of the second Principle. What he had really managed to do was the derivation of the second Principle from an original and questionable alliance between mechanics and probability.

Boltzmann 1877 paper raised a new and more widespread debate, mainly after Poincaré's recurrence theorem became known to the scientific community. Both the criticism of the young mathematician Zermelo, and the debate which involved some British physicists and the journal *Nature*, are well known to historians. According to Poincaré, 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 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"?²⁰

²⁰ Poincaré H. 1893, pp. 534-7. 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.

4. The mathematical physics of French engineers

Besides the pathway to Thermodynamics undertaken by Maxwell and Boltzmann, there was a different pathway, and French scientists had an important part in it. The most interesting difference between them dealt with the relationship between Thermodynamics and Mechanics. Following the former, microscopic mechanical models, mixed with some extra-mechanical hypothesis, were expected to account for the thermodynamic behaviour of macroscopic systems. Following the latter, a general mathematical theory had to be pursued, without any reference to whatever kind of microscopic structure underlying the physical system under consideration. The meaning of expressions like “mechanical theory of heat” stood in the formal similarity between the mathematical structure of Thermodynamics and the mathematical structure of Mechanics, rather than in mechanical models of heat.

In 1851, Ferdinand Reech, Navy engineer and director of the *École du Genie Maritime*, sent a short paper to the *Comptes Rendus* de l’Académie des Sciences, in the section *Mathématiques Appliquées*. He reminded the reader of Carnot’s 1924 essay and Clapeyron’s 1830 paper, specifically the mathematical law

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

wherein 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. Both Carnot and Clapeyron had assumed that the motive force stemmed from the transfer of that amount q of heat from a source A' at the temperature t' to a source A at the lower temperature t . The transfer of caloric – Reech remarked – could not transform into mechanical force completely, for “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:

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

In a long essay Reech published in the *Journal de Mathématiques pures et appliquées* in 1853, and reprinted as the volume *Théorie générale des effets dynamiques de la chaleur* the following year, he mentioned Joule, Thompson [sic], Rankine, Mayer and Clausius' recent researches. He regretted that “mere hypotheses were given so great importance”, and claimed that “the logic consistency of the reasoning” should have been restored. The “new point of view” he announced was developed in that volume and 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 aimed at deriving the most general and complete amount of “formulae” consistent with “the totality of future experiments” undertaken by physicists.²

His theory was quite a mathematical one indeed. He started from the above equation, rewritten in an integral form,

$$S = q' \Gamma(t') - q \Gamma(t) = \int_t^{t'} \frac{d[q \Gamma(t)]}{dt} dt,$$

and stressed that the function $\Gamma(t)$ was the same “for all bodies in nature”. The above equation replaced Carnot and Clapeyron's equation

¹ Reech F. 1851, pp. 567-8 and 570. The role of Reech was emphasised by A.C. Truesdell. In 1977, he dedicated the book written together with S. Bharatha to the memory of Carnot, Reech, and Duhem: “May this tractate be received as an expression of respectful gratitude for the legacy of the great French thermodynamicists”. See also chapters 8 and 14 in the same book (Truesdell C., Bharatha S. 1977). He defined a textbook Reech published in 1868 as “the clearest presentation of the subject I have ever seen”. (Truesdell A.C. 1980, p. 299). See also *Ibidem*, chapter 10, which is devoted to a modern rephrasing of Reech theories.

² Reech F. 1854, p. 1, and Reech F. 1856, p. 61. In a footnote he stressed once again the mathematical character of his researches: “Mon but n'a jamais été de m'occuper de ces matières comme physicien, mais seulement comme logicien, particulièrement en ce qui concerne le perfectionnement de la théorie des machines motrices, ...” (Reech F. 1856, pp. 65-6)

$$(1) \quad S = q \int_t^{t'} \frac{dt}{C},$$

which was consistent with the hypothesis $q' = q$, provided that C represented a universal function of temperature.

Then Reech made reference to two different scientific traditions, in order to show that

$$(3) \quad \Gamma(t) = \text{const.}$$

He borrowed from the tradition of kinetic theories of heat the assumption that “heat would be equivalent to the living force”: in this case, S and q have the same physical dimension. The function $\Gamma(t)$ cannot therefore be anything else but a constant quantity. Then he borrowed from Fourier tradition the mathematical theory of heat conduction. In this case “there is neither production of work nor any kind of waste”, and therefore $q' = q$ and $S = 0$. As a consequence,

$$q' \Gamma(t') = q \Gamma(t), \quad \Gamma(t') = \Gamma(t) = \text{const.}$$

and therefore

$$(4) \quad S = G(q' - q)$$

It is worth remarking the integration Reech put forward between the different traditions of the science of heat: Fourier flow of heat without mechanical work, Carnot transformation of heat into mechanical work without free flow of heat, and Joule equivalence between heat and mechanical work.³

³ Reech F. 1856, pp. 59-60.

He tried to generalize the mathematical treatment of Carnot cycle; the internal surface of the closed line representing the cycle in a Cartesian plane corresponded to S . Then he assumed that the isothermal transformations were expressed by the equations

$$\varphi(v, p) = t, \quad \varphi(v, p) = t',$$

and the adiabatic ones by

$$\psi(v, p) = u, \quad \psi(v, p) = u'.$$

For the amount of heat q and q' he assumed functions of the general kind

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

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

$$(7) \quad q = \int_u^{u'} \gamma(t) du = \gamma(t)(u' - u), \quad q' = \int_u^{u'} \gamma(t') du = \gamma(t')(u' - u).$$

As a consequence, what Reech called “Causius’ second theorem” followed:

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

From the equations (4) and (7),

$$(8) \quad S = G(q' - q) = G(u' - u) [\gamma(t') - \gamma(t)] = G(u' - u) \int_u^{u'} \gamma(t') dt'.$$

The comparison between Reech equation (8) and Carnot-Clapeyron equation

$$(1) \quad S = q \int_t^{t'} \frac{dt}{C}$$

offered a meaningful correspondence. The abstract term $G(u' - u)$ played in the former the same role the quantity of heat q played in the latter, and the universal function $\gamma(t)$ played the role of $1/C$.⁴

After thirteen years, another French engineer took the road 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 consistent and unifying mathematical theory. He started from the two principle involving energy and entropy. An 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”. He remarked that the last two effects could not be identified separately. Only some kind of hypotheses would allow us to distinguish between work and heat inside the body. From the mathematical point of view, a single function U accounted for the sum of “mechanical and thermal effects, which merge with each other due to the principle of equivalence between heat and work”. Massieu did not further explain this asymmetry between macroscopic and microscopic level: why should we distinguish heat from work at the macroscopic level, and should not at the microscopic? The fact is that the transfer of heat dQ was different from what Massieu labelled “sensible heat” and - he reported - “many scholars call internal heat”.

If $p dv$ was the external work, it was “thermally equivalent” to $A p dv$, wherein A was the well-known conversion factor between mechanical and thermal measures. The first principle could therefore be expressed by the equation

⁴ Reech F. 1856, pp. 60-1 and 65.

$$(1) \quad dQ = dU + A p dv .$$

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”. The function S was nothing else but Clausius’ entropy.⁵

After having chosen v and t (volume and temperature) as independent variables, from the mathematical point of view,

$$(2) \quad dQ = \frac{\partial U}{\partial t} dt + \frac{\partial U}{\partial v} dv + A p dv = \frac{\partial U}{\partial t} dt + \left(\frac{\partial U}{\partial v} + A p \right) dv ,$$

and therefore

$$(3) \quad dS = \frac{dQ}{T} = \frac{1}{T} \frac{\partial U}{\partial t} dt + \frac{1}{T} \left(\frac{\partial U}{\partial v} + A p \right) dv .$$

Being S a complete differential,

$$\frac{\partial}{\partial v} \left(\frac{1}{T} \frac{\partial U}{\partial t} \right) = \frac{\partial}{\partial t} \left[\frac{1}{T} \left(\frac{\partial U}{\partial v} + A p \right) \right] .$$

Massieu skipped some mathematical steps, which we can perform following his logical pathway:

⁵ Massieu F. 1869a, p. 858.

$$\frac{1}{T} \frac{\partial^2 U}{\partial v \partial t} = -\frac{1}{T^2} \frac{\partial U}{\partial v} + \frac{1}{T} \frac{\partial^2 U}{\partial v \partial t} - \frac{1}{T^2} A p + \frac{A}{T} \frac{\partial p}{\partial t},$$

$$\frac{1}{T^2} \frac{\partial U}{\partial v} = -\frac{1}{T^2} A p + \frac{A}{T} \frac{\partial p}{\partial t},$$

$$(4) \quad \frac{\partial}{\partial v} \left(\frac{U}{T^2} \right) = \frac{\partial}{\partial t} \left(\frac{A p}{T} \right).$$

This means that we can define another function ψ whose differential

$$(5) \quad d\psi = \frac{U}{T^2} dt + \frac{A p}{T} dv$$

is 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.⁶ Two slightly different deductions are outlined in the short paper and in some pages he added subsequently. From equation (5),

$$\frac{\partial \psi}{\partial t} = \frac{U}{T^2} \quad \text{and} \quad \frac{\partial \psi}{\partial v} = \frac{A p}{T}.$$

Therefore

$$U = T^2 \frac{\partial \psi}{\partial t} \quad \text{and} \quad p = \frac{T}{A} \frac{\partial \psi}{\partial v}.$$

If

⁶ Massieu F. 1869a, p. 859. In his paper, Massieu did not distinguish partial from total derivatives.

$$dS = \frac{dQ}{T} = \frac{1}{T} \frac{\partial U}{\partial t} dt + \frac{1}{T} \left(\frac{\partial U}{\partial v} + A p \right) dv ,$$

then

$$dS = \frac{1}{T} \frac{\partial \left(T^2 \frac{\partial \psi}{\partial t} \right)}{\partial t} dt + \frac{1}{T} \left(\frac{\partial \left(T^2 \frac{\partial \psi}{\partial t} \right)}{\partial v} + T \frac{\partial \psi}{\partial v} \right) dv ,$$

$$dS = \frac{1}{T} \left[2T \frac{\partial \psi}{\partial t} + T^2 \frac{\partial^2 \psi}{\partial t^2} \right] dt + \frac{1}{T} \left(T^2 \frac{\partial^2 \psi}{\partial v \partial t} + T \frac{\partial \psi}{\partial v} \right) dv ,$$

$$dS = \left[\frac{\partial \psi}{\partial t} + \frac{\partial \psi}{\partial t} + T \frac{\partial^2 \psi}{\partial t^2} \right] dt + \left(T \frac{\partial^2 \psi}{\partial v \partial t} + \frac{\partial \psi}{\partial v} \right) dv ,$$

$$dS = \left[\frac{\partial}{\partial t} \left(\psi + T \frac{\partial \psi}{\partial t} \right) \right] dt + \left[\frac{\partial}{\partial v} \left(\psi + T \frac{\partial \psi}{\partial t} \right) \right] dv .$$

At the end,

$$S = \psi + T \frac{\partial \psi}{\partial t} ,$$

and therefore S has been expressed in terms of the *characteristic function* ψ .

Remembering that

$$\frac{\partial \psi}{\partial t} = \frac{U}{T^2} ,$$

we can write

$$S = \psi + \frac{U}{T}.$$

This means that not only can U and S be expressed in terms of the function ψ , but ψ can be expressed in terms of U and S :

$$\psi = S - \frac{U}{T}.$$

A more synthetic expression for S is

$$S = \frac{\partial}{\partial t}(T\psi).^7$$

Then Massieu introduced a second *characteristic function* ψ' in terms of the two variables t and p . He first defined a new function

$$U' = U + A p v.$$

If

$$dU' = dU + A p dv + A v dp,$$

then

⁷ Massieu F. 1869b, p. 1058.

$$dU = dU' - A p dv - A v dp$$

and

$$dQ = dU + A p dv = dU' - A p dv - A v dp + A p dv = dU' - A v dp.$$

If t and p are the two independent variables,

$$dQ = \frac{\partial U'}{\partial t} dt + \frac{\partial U'}{\partial p} dp - A v dp = \frac{\partial U'}{\partial t} dt + \left(\frac{\partial U'}{\partial p} - A v \right) dp,$$

and therefore

$$dS = \frac{dQ}{T} = \frac{1}{T} \frac{\partial U'}{\partial t} dt + \frac{1}{T} \left(\frac{\partial U'}{\partial p} - A v \right) dp.$$

The above deductive engine can be put in action for the search of ψ' . Being S a complete differential,

$$\frac{\partial}{\partial p} \left(\frac{1}{T} \frac{\partial U'}{\partial t} \right) = \frac{\partial}{\partial t} \left[\frac{1}{T} \left(\frac{\partial U'}{\partial p} - A v \right) \right].$$

The mathematical steps are similar to those undertaken in the search of ψ :

$$\frac{1}{T} \frac{\partial^2 U'}{\partial p \partial t} = - \frac{1}{T^2} \frac{\partial U'}{\partial p} + \frac{1}{T} \frac{\partial^2 U}{\partial p \partial t} + \frac{1}{T^2} A v - \frac{A}{T} \frac{\partial v}{\partial t},$$

$$\frac{1}{T^2} \frac{\partial U'}{\partial p} = \frac{1}{T^2} A v - \frac{A}{T} \frac{\partial v}{\partial t},$$

$$\frac{\partial}{\partial p} \left(\frac{U'}{T^2} \right) = - \frac{\partial}{\partial t} \left(\frac{A v}{T} \right).$$

This means that we can define a new function ψ' whose differential

$$d\psi' = \frac{U'}{T^2} dt - \frac{A v}{T} dp$$

is a complete differential of p and t : ψ' is Massieu second “*characteristic function*”.

This also means that

$$\frac{\partial \psi'}{\partial t} = \frac{U'}{T^2} \quad \text{and} \quad \frac{\partial \psi'}{\partial p} = - \frac{A v}{T},$$

or

$$U' = T^2 \frac{\partial \psi'}{\partial t} \quad \text{and} \quad v = - \frac{T}{A} \frac{\partial \psi'}{\partial p}.^8$$

At this point let me skip all the mathematical steps leading from

$$dQ = dU' - A v dp \quad \text{and} \quad dS = \frac{dU'}{T} - \frac{A v dp}{T}$$

to

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

⁸ Massieu F. 1869b, p. 1059.

In the case of ideal gases,

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

This means that, except for a constant, ψ and ψ' are the same function.⁹

Not only did Massieu claim that U , p , v , Q and S could be derived by 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' did. 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.¹⁰

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 even a 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 began to be filled just by the unifying power of Thermodynamics, which he identified with “the mechanical theory of heat”.¹¹ It is worth remarking that, in Massieu’s theoretical and meta-theoretical context, “mechanical” did not mean microscopic mechanical models in the sense of Maxwell and Boltzmann, but a mathematical approach on the track of the mathematical generalisation of Mechanics, which had been undertaken by French mathematicians at the turn of the nineteenth century.

This “mechanical theory of heat” could allow mathematicians and engineer to “settle a link between similar properties of different bodies”. Thermodynamics could rely on a consistent set of general and specific laws, and his “characteristic functions” could be

⁹ Massieu F. 1869b, p. 1060.

¹⁰ Massieu F. 1869b, pp. 860 and 1060-1.

¹¹ 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.”

looked upon as the mathematical and conceptual link between the general and specific laws.

“Les principe fondamentaux de la thermodynamique peuvent être représentés par deux équations générales applicable 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 compatible 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.”¹²

He acknowledged that, for the successful application of his theoretical procedure, the scientists should have gone on asking nature in order to receive those “data which we do not have got yet”. At the same time, the engineer Massieu appreciated a theoretical practice which “goes beyond the observation”, and shows 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 are functions of them. The relationship between the “internal heat” or “internal energy” U and Q was given by the usual fundamental law

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

which could be generalised into

¹² Massieu F. 1876, pp. 2-3.

$$Q = U - U_0 + A \mathfrak{T}_e + A \left(\frac{\sum m w^2}{2} - \frac{\sum m w_0^2}{2} \right).$$

The term $\mathfrak{T}_e$ represented “the external work performed by the body”, and the bracketed term represented the difference between final and initial living force corresponding to the “sensible motion” of the body.¹³

In reversible cyclic transformations,

$$Q = A \mathfrak{T}_e \quad \text{and} \quad \int \frac{dQ}{T} = 0.$$

According to Massieu, the two equations “express the two general principles of the mechanical theory of heat”. The two state functions U and S , corresponding to two complete differentials, were not mutually independent: they could be derived by a sole function, namely his “characteristic function”.¹⁴

In this essay, the deduction of the characteristic function is shorter and simpler than in the previous paper. From

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

we have

$$T dS = dU + A p dv.$$

The addition of the term $S dt = S dT$ to both members gives

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

¹³ Massieu F. 1876, pp. 3-5.

¹⁴ Massieu F. 1876, pp. 6-8.

or

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

Since the first member is a total differential, so is the second, and we can write

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

where the function H, is nothing else but the function ψ of the previous paper.
Moreover

$$S = \frac{dH}{dT} ,$$

$$A p = \frac{dH}{dv}$$

$$U = ST - H$$

$$U = T \frac{dH}{dT} - H .^{15}$$

An important feature of ideal gases could be derived by the mathematical properties of the characteristic function: internal energy cannot depend on volume but only on temperature. Expressions for k , k' , β , β' , and the coefficient of compressibility

$$\varepsilon = - \frac{1}{v} \frac{dv}{dp}$$

¹⁵ Massieu F. 1876, pp. 9-10.

were given in terms of H and its derivatives. Other features of ideal gases, were derived by Massieu in the following pages:

$$k - k' = A R, \quad \frac{dk}{dv} = \frac{dk'}{dv} = 0, \quad \frac{dk}{dt} = \frac{dk'}{dt}.$$

Explicit expressions for the characteristic function in terms of the independent variables t and v were given for ideal gases and saturated vapours.¹⁶

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 double 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.¹⁷

On the other hand, all parameters and specific equations describing the specific system could be derived by the knowledge of H' : in Massieu's words, from a given stage on, "it is only a matter of computation". The mathematical engine allowed the researcher to check if specific laws were consistent with the whole of the theoretical structure of Thermodynamics.

¹⁶ Massieu F. 1876, pp. 10-25.

¹⁷ Massieu F. 1876, p. 29.

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.¹⁸

The second half 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 the specific heat. At the end Massieu hinted at a very sensitive issue: 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.¹⁹

¹⁸ Massieu F. 1876, p. 43.

¹⁹ 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."

5. A Thermodynamic world-view

In 1855, a Scottish engineer, already Fellow of the *Royal Society* since 1853, who had just been appointed to the chair of civil engineering in Glasgow, Macquorn Rankine, published a paper in the *Proceedings* of the *Philosophical Society of Glasgow*, wherein he put forward a unified account of mechanical and thermal effects. Rankine design was far beyond Reech's: his fruitful integration between the technical tradition of thermal engines and the tradition of mathematical physics led to an original re-interpretation and unification of physics. The headline of the paper, "*Outline of the Science of Energetics*" could appear a bit astonishing in the context of mid-nineteenth-century physics. Rankine himself explained the term "Energetics" in the seventh section of the paper, "Nature of the Science of Energetics". The term contained the reference to both the universality of the concept of energy, and the design of generalisation of physics.

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.¹

From the outset, both theoretical and meta-theoretical commitments emerges from Rankine paper. At first he identified two subsequent steps in scientific practice: if the former consisted in deriving "formal laws" from experimental data on "an entire class of phenomena", the latter 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

¹ Rankine M. 1855, in Rankine M. 1881, pp. 213-4.

scientific practice: the “ABSTRACTIVE” and the “HYPOTHETICAL”. In the former, scientists confined themselves to a mathematical re-interpretation and classification of phenomena in physics; in the latter, they relied on models and analogies, in order to catch the intimate nature of phenomena or hidden structures underlying them.

According to the ABSTRACTIVE method, a class of object or phenomena is defined by describing, or otherwise making to be understood, and assigning a name or symbol to, that assemblage of properties which is common to all the objects or phenomena composing the class, as perceived by the senses, without introducing anything hypothetical.

According to the HYPOTHETICAL method, a class of object or phenomena is defined, according to a conjectural conception of their nature, as being constituted, in a manner not apparent to the senses, by a modification of some other class of objects or phenomena whose laws are already known. Should the consequences of such a hypothetical definition be found to be in accordance with the results of observation and experiment, it serves as the means of deducing the laws of one class of objects or phenomena from those of another.²

Obviously, Rankine reference to the possibility of doing science without making recourse to “anything hypothetical” is not consistent with whatever kind of actual scientific practice. It seems more an idealisation or a rhetoric contrivance than an actual design. Moreover, the statement that science should be purified by hypotheses is, at least, a definite meta-theoretical hypothesis. Nevertheless, the distinction put forward by Rankine was not meaningless, and it would have been re-discovered at the end of the century in the context of the emerging theoretical physics. Rankine’s 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

² Rankine M. 1855, in Rankine M. 1881, p. 210.

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 of the “abstractive theory”.³

The tradition of mechanics had provided scientists with a plenty of “*mechanical*” models or “hypotheses”. Rankine explained what a mechanical model exactly was with the help of examples well-known to scientists.

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

The hypothetical motions and forces are sometimes ascribed to *hypothetical bodies*, such as the luminiferous ether; sometimes to *hypothetical parts*, whereof tangible bodies are conjecturally defined to consist, such as atoms, atomic nuclei with elastic atmospheres, and the like.⁴

In reality, Rankine did not disdain the mechanical models. In 1851 he had devoted a paper to the relationship between heat and centrifugal forces arising from microscopic vortices. In 1853, in a paper on the mechanical (in a macroscopic, thermodynamic sense) action of heat, he had made reference to his “supposition” of “molecular vortices”, to the hypothesis that “heat consists in the revolutions of what are called

³ Rankine M. 1855, in Rankine M. 1881, pp. 210 and 213. Rankine choice of labelling “*objective*” and “*subjective*” the two interpretations of the “hypothetical method” seems to me quite misleading.

⁴ Rankine M. 1855, in Rankine M. 1881, p. 211.

molecular vortices”, more specifically that “the elasticity arising from heat is in fact centrifugal force”.⁵

At the same time, the tradition of mechanics offered a structural analogy 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”, as “names” referring to “very comprehensive classes of objects and phenomena” rather than to “any particular object” or “any particular phenomena”. He realised 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 tend to vary”. It had to be distinguished by the concept of “*Complex Accident*”, which corresponded to “the whole condition or state of a substance”: “thermic condition” and “condition of strain” were complex accidents for they required more than one independent variables (accident) to be specified.⁶

At the end, the concept of work was a key concept in Rankine theory.

“*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

⁵ See Rankine M. 1853, in Rankine M. 1881, p. 310. In his 1851 paper, he reminded the reader about a model he had put forward the year before, before putting forward a mathematical generalisation. See also 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.”

⁶ Rankine M. 1855, in Rankine M. 1881, pp. 214-6.

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

Work is represented geometrically by the area of a curve, whereof the abscissa represents the passive accident, and the ordinate, the effort.⁷

The generalisation of the concept of work entailed the generalisation of the concept of energy, which was the core of Rankine energetics. The concept of “*Actual energy*” was a generalisation of mechanical *living force*: it included “heat, light, electric current”, and so on. The concept of “*Potential energy*” was extended far beyond gravitation, elasticity, electricity and magnetism. It included “chemical affinity of uncombined elements”, and “mutual actions of bodies, and parts of bodies” in general:

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

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

$$W = X dx + Y dy + Z dz +^8$$

Rankine was aware that the concept of potential energy was problematic, and that a sharp split between actual and potential energy could not catch the complexity of some phenomena. The fact is actual energy “may possess the characteristics of potential energy also”: it can 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

⁷ Rankine M. 1855, in Rankine M. 1881, pp. 216-7.

⁸ Rankine M. 1855, in Rankine M. 1881, pp. 217 and 222.

accompanied by a tendency to expand”, namely “an effort to increase the volume of the receptacle” containing the elastic fluid. The concept of potential energy was more suitable for the case of “mutual actions” or forces acting symmetrically on pairs of bodies.⁹

Rankine submitted energy and work, the key concepts of his Energetics, to three “*Axioms*”. The first concerned the universality and convertibility of energy: these two features were treated separately although being tightly interwoven. Universality was expressed in two ways: “*any kind of energy may be made the means of performing any kind of work*”, or, more formally, “*All kinds of Work and Energy are Homogeneous*”. This homogeneity was remarkable: although “efforts and passive accidents to which the branches of physics relate are varied and heterogeneous”, all works and energies, the result of the multiplication between every effort and the corresponding accident, were physical quantity of the same kind. It was just this homogeneity which allowed energy to be transformed from one form into another. Rankine looked upon transformation and transference as different aspects of the same property.

... to *transform energy*, means to employ energy depending on accidents of one kind in putting a substance into a state of energy depending on accidents of another kind; and to *transfer energy*, means to employ the energy of one substance in putting another substance in a 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.¹⁰

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

⁹ Rankine M. 1855, in Rankine 1881, p. 218. In 1867, in response to John Herschel 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” would have been 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 knowledge of classic philosophy see Tait P. G. 1880, p. xxi.

¹⁰ Rankine M. 1855, in Rankine M. 1881, p. 218.

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 first and 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".¹¹

Rankine third axiom is quite difficult to explain, but it is definitely the most original, and allows us to better understand his Energetics. Rankine whole design required the re-interpretation of thermodynamic transformations in terms of transformations of actual energy, and then a powerful 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 net of assumptions and derivations, we must first browse two papers he had read before the Philosophical Society of Glasgow in January 1853, and then return to his 1855 paper. In the second 1853 paper, whose title is "On the General Law of the Transformation of Energy", 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 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: 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 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 was to be distinguished from the fluxes of heat between the substance and the surrounding bodies. The former was "the heat possessed by the body" Q , and the pressure P was a function of it.¹²

¹¹ Rankine M. 1855, in Rankine M. 1881, p. 218. Rankine traced back the cosmological implication of the theoretical argument to Newton's *Principia*, in particular the "Scolium to the Laws of Motion".

¹² Rankine M. 1853, in Rankine M. 1881, p. 311. The identification of heat or "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.

The core of the computation was the determination of “the portion of the mechanical power $P dV$ which is the effect of heat: in other words, the fraction of actual energy transformed into work. Rankine defined “the development of power for the expansion dV , caused by each indefinitely small portion dQ of the total heat possessed by the body” as

$$dQ \times \frac{dP}{dQ} dV.$$

The whole “mechanical power” was therefore expressed by

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

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

$$Q \times \frac{dP}{dQ} dV - P dV = \left(Q \times \frac{dP}{dQ} - P \right) dV.^{13}$$

Molecular attraction – Rankine remarked – must be derived by a potential S , which is a function of V and Q . In this case, the above equation implies that

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

The integration with regard V leads to

¹³ Rankine M. 1853, in Rankine M. 1881, p. 312.

$$S = \int \left(Q \times \frac{dP}{dQ} - P \right) dV + \phi(Q),$$

where the function ϕ depends on Q only. The derivation with regard Q leads to

$$\frac{\partial S}{\partial Q} = \int \left(\frac{\partial Q}{\partial Q} \times \frac{dP}{dQ} + Q \times \frac{d^2 P}{dQ^2} - \frac{dP}{dQ} \right) dV + \phi'(Q)$$

$$\frac{\partial S}{\partial Q} dQ = \left[Q \int \left(\frac{d^2 P}{dQ^2} \right) dV + \phi'(Q) \right] dQ^{14}$$

In the framework of Rankine thermodynamics, the whole heat “which is consumed” would consist 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”. The whole consumed heat would correspond to the flux of heat coming from outside, which we could call q . From the mathematical point of view,

$$\begin{aligned} dq &= dQ + dS + P dV = dQ + \frac{\partial S}{\partial Q} dQ + \frac{\partial S}{\partial Q} dV + P dV = \left(1 + \frac{\partial S}{\partial Q} \right) dQ + \left(\frac{\partial S}{\partial Q} + P \right) dV = \\ &= \left[1 + Q \int \left(\frac{d^2 P}{dQ^2} \right) dV + \phi'(Q) \right] dQ + \left[Q \times \frac{dP}{dQ} - P + P \right] dV = \\ &= \left[1 + Q \int \left(\frac{d^2 P}{dQ^2} \right) dV + \phi'(Q) \right] dQ + \left[Q \times \frac{dP}{dQ} \right] dV \end{aligned}$$

Not only can this sum be divided into sensible heat and latent heat, but also divided into the internal heat and work, on the one hand, and the 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”,

¹⁴ Rankine M. 1853, in Rankine M. 1881, pp. 312-3.

both in form of heat or mechanical power, “to make it pass from a one volume and temperature to another”. In other words, it was a state function.¹⁵

The previous paper wherein he had qualified the function Ψ is the paper he had published in 1851 on the centrifugal theory of elasticity and its application to the theory of heat.

This quantity consists partly of expansive or compressive power, and partly of heat, in proportions depending on the mode in which the intermediate changes of temperature and volume take place; but the total amount is independent of these changes.

*Hence, if a body be made to pass through a variety of changes of temperature and volume, and at length be brought back to its primitive volume and temperature, the algebraical sum of the portions of power applied to and evolved from the body, whether in the form of expansion or compression, or in that of heat, is equal to zero.*¹⁶

Going back to Rankine 1853 paper, the balance of energy, and the computation of the fraction of actual energy transformed into macroscopic work, led to both applications and abstract generalisations. With regard to applications, Rankine remarked that the thermal engine with the best efficiency must correspond to a cycle operating by two isothermal and two adiabatic transformations, just as in Carnot model.¹⁷

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;

¹⁵ Rankine M. 1853, in Rankine M. 1881, pp. 313 and 317.

¹⁶ Rankine M. 1851, in Rankine M. 1881, p. 62.

¹⁷ Rankine M. 1853, 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

$P dV$ 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 $P dV$ 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 $\int P dV$, whatsoever those forms may be, when no other form of energy interferes.¹⁸

This generalisation leads to the third axiom Rankine tried to explain with great detail in his 1855 paper, the axiom he labelled “GENERAL LAW OF THE TRANSFORMATION OF ENERGY”. Returning to this paper, it is worth remarking that he introduced a continuous representation of actual energy: “a quantity Q , of a particular kind of actual energy, uniformly distributed”. In reality, under the label “transformation” he encompassed both transformations from actual energy into work and exchanges of actual energy. If the first process lead 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 corresponding to a given accident x :

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

¹⁸ Rankine M. 1853, in Rankine M. 1881, p. 318.

In general, when the work W depends on many forces $X, Y, Z, \dots$

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

The above expression can be integrated in order to obtain dW/dQ or H . In the first case,

$$d \left(\frac{dW}{dQ} \right) = \frac{dH}{Q}; \quad \frac{dW}{dQ} = \int \frac{dH}{Q} = F.$$

The function F was called “METAMORPHIC FUNCTION” by Rankine: it corresponded to the fraction of actual energy transformed into work. In the second case,

$$H = \int Q d \left(\frac{dW}{dQ} \right) = \int Q dF$$

corresponded to the amount of actual energy transformed into work.¹⁹

With regard to exchanges of actual energy between two substances A and B , Rankine tried to generalise the mathematical interpretation of processes of 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”

$$Q \frac{dX}{dQ}.$$

¹⁹ Rankine M. 1855, in Rankine M. 1881, pp. 220-2.

Then he wrote down the conditions of equilibrium: the equilibrium was interpreted as the final consequence of the fluxes of actual energy:

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

As a consequence,

$$\frac{dQ_A}{Q_A} = \frac{dQ_B}{Q_B},$$

and the subsequent integration yielded

$$\begin{aligned} \log(Q_A) - \log(Q_{A_0}) &= \log(Q_B) - \log(Q_{B_0}), \quad \log(Q_A) - \log(Q_B) = \log(Q_{A_0}) - \log(Q_{B_0}), \\ \log\left(\frac{Q_A}{Q_B}\right) &= \log\left(\frac{Q_{A_0}}{Q_{B_0}}\right), \quad \frac{Q_A}{Q_B} = \frac{Q_{A_0}}{Q_{B_0}} = \frac{K_A}{K_B}, \quad \frac{Q_A}{Q_B} = \frac{K_A}{K_B} = \theta. \end{aligned}$$

The constants K_A and K_B were the generalisation of specific heats: Rankine named them “SPECIFIC ACTUAL ENERGIES” of A and B . The function θ , which “expresses the condition of equilibrium of the actual energy Q between them“, was labelled “METABATIC FUNCTION”. It was a generalisation of the concept of “*absolute temperature*”.²⁰

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 free flow of heat. They had been translated into a mathematical theory from Carnot and Fourier respectively. At the time Rankine wrote his paper on Energetics, the two theory represented distinct sections of the theory of heat. It is quite remarkable that Rankine had dared a unified mathematical interpretation of both processes.

²⁰ Rankine M. 1855, in Rankine M. 1881, pp. 223-5.

The generalisation of Thermodynamics was further carried on by Rankine, and a second “METAMORPHIC FUNCTION” introduced, in accordance with the proportionality just established between Q and θ . Indeed,

$$Q \frac{\partial}{\partial Q} = \theta \frac{\partial}{\partial \theta}$$

and therefore

$$dH = \theta d\left(\frac{dW}{d\theta}\right).$$

If we define a new metamorphic function ϕ proportional to F ,

$$\phi = KF \quad \text{or} \quad F = \frac{\phi}{K},$$

then

$$H = \int Q dF = \int K\theta d\left(\frac{\phi}{K}\right) = \int \theta d\phi.$$

In other words, the integral relationship between the metabatic and metamorphic functions θ and ϕ gives “the quantity of actual energy of a given kind Q transformed to the kind of work W during any finite variation of accidents”.²¹

Metabatic and metamorphic functions allowed Rankine to re-interpret the operation of engines in general, on the track of Carnot ideal engine.

In a perfect engine the cycle of variations is thus:

²¹ Rankine M. 1855, in Rankine M. 1881, pp. 225-6.

- 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 $(\theta_1 - \theta_0) \Delta\phi$.²²

Rankine tried to unify the conceptual and mathematical approach to the two fundamental processes: transformations of actual energy into work, and “*equable diffusion* of actual energy”. The key concept was “*irreversibility*”, namely the 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.²³

²² 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”.

²³ Rankine M. 1855, in Rankine M. 1881, p. 227. 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”.

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 were “*the times in which equal quantities of the same kind of work are performed by equal and similar substances*”.²⁴

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, able to encompass the whole of phenomena. This confidence in the generality and universality of a physical theory stemmed from an open-minded attitude, from the awareness that the scientific practice is an 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”.²⁵

²⁴ Rankine M. 1855, in Rankine M. 1881, p. 227.

²⁵ Rankine M. 1855, in Rankine M. 1881, p. 228.

6. *From mechanical to thermodynamic equilibrium*

An abstract approach to Thermodynamics, and the choice of wide-scope generalisations were also the hallmarks of J. Willard Gibbs, an American engineer who had accomplished his scientific training in Paris, Berlin and Heidelberg. He held the chair of mathematical physics at Yale since 1871, and published a series of fundamental papers under the common title “On the equilibrium of heterogeneous substances” in the *Transactions of the Connecticut Academy* since 1875 till 1878.

In the first lines of his thick collection, Gibbs stated that he was interested in a very wide subject, although based only on two fundamental principles. The subject was “the laws which govern any material system”, and the two principles involved the two basic entities energy and entropy, whose “varying values” would “characterize in all that is essential” the transformations of that system. His more general mechanics dealt with a “thermodynamic system”, because “such as all material systems are”: Thermodynamics was looked upon as a generalisation of the 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 is a function “which expresses the capability of the system for this kind of action”, and the condition of equilibrium requires 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 constant energy ε , and the second under the condition of 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,

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

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 corresponds to the maximum entropy, whereas in transformations taking place at constant entropy, the equilibrium corresponds to the minimum energy. The second form of the criterion of equilibrium seemed to Gibbs more suitable for applications. As first application, he considered “a mass of matter of various kinds enclosed in a rigid and fixed envelope”, 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

$$d\varepsilon = t d\eta - p dv \quad (11),$$

which is nothing else but the first principle of thermodynamics. The first term in the second member is “the heat received”, and the second term is “the work done”. The equation is written in order to emphasize that homogeneous mass’ “energy ε is a function of its entropy η , and its volume v ”; as usual, “ t denotes the absolute temperature of the mass, and p its pressure”. As Gibbs was not confining himself to “simply mechanical systems”, he let “the various substances $S_1, S_2, \dots S_n$ of which the mass is composed” change their mass. As a consequence, the energy ε of the

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.

homogeneous component of the system can also depend on the corresponding variable masses $m_1, m_2, \dots m_n$:

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n \quad (12)$$

wherein $\mu_1, \mu_2, \dots \mu_n$ denote “the differential coefficients of ε taken with respect to $m_1, m_2, \dots m_n$ ”. In general, Gibbs remarked, it would have been necessary to take also into account “component substances which do not initially occur in the homogeneous mass considered”.⁴ It is becoming increasingly apparent that Gibbs’ generalized mechanics is intended to account for chemical as well as for physical phenomena. The “general condition of equilibrium” for “the whole mass” was synthetically written as

$$\delta\varepsilon' + \delta\varepsilon'' + etc. \geq 0 \quad (14)$$

and analytically as

$$\begin{aligned} & t' d\eta' - p' dv' + \mu'_1 dm'_1 + \mu'_2 dm'_2 + \dots \mu'_n dm'_n \\ & + t'' d\eta'' - p'' dv'' + \mu''_1 dm''_1 + \mu''_2 dm''_2 + \dots \mu''_n dm''_n \cdot \quad (15) \\ & + etc. \geq 0 \end{aligned}$$

Gibbs showed that, for the equilibrium, “it is evidently necessary and sufficient that” the conditions of thermal, mechanical and chemical equilibrium were simultaneously fulfilled. In detail:

$$\begin{aligned} t' &= t'' = t''' = etc. \\ p' &= p'' = p''' = etc. \\ \mu'_1 &= \mu''_1 = \mu'''_1 = etc. \quad \mu'_2 = \mu''_2 = \mu'''_2 = etc. \quad \dots \quad \mu'_n = \mu''_n = \mu'''_n = etc. \end{aligned} \quad (19, 20, 21)$$

⁴ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 63.

To the coefficients μ_x Gibbs attributed the qualification of “potential for the substance S_x ”.⁵ Each homogeneous sub-set depends on the $(n+2)$ variables $t, v, m_1, m_2, \dots, m_n$, and the whole system depends on $(n+2)v$, wherein v is “the number of homogeneous parts into which the whole mass is divided”. The last series of equations involving t, p , and $\mu_1, \mu_2, \dots, \mu_n$ contains exactly $(v-1)(n+2)$ conditions among the $(n+2)v$ variables. The remaining unknown variables are $(n+2)$. If the volume of “the whole mass” and “the total quantities of the various substances” are known, namely additional $(n+1)$ conditions are available. It therefore remains only one unknown variable, but the knowledge of “the total energy of the given mass”, or alternatively “its total entropy”, would allow us to have “as many equations as there are independents variables”.⁶ Apart from the algebraic problem, which Gibbs showed to be solvable, from the physical point of view we have a very general procedure, which allows us to process mechanical, thermal and chemical properties of a given physical system.

In the following pages, Gibbs proceeded to widen the scope of his *thermodynamic mechanics*. If the substances $S_1, S_2, \dots, S_n$ “are not all independent of each other” but “some of them can be formed out of others”, other conditions are required. If $\Sigma_a, \Sigma_b, \Sigma_k \dots$ denote the units of certain substances $S_a, S_b, S_k \dots$ among the $S_1, S_2, \dots, S_n$, which undergo this kind of qualitative transformation, a new kind of “qualitative as well as quantitative equivalence” must be satisfied:

$$\alpha\Sigma_a + \beta\Sigma_b + etc. = \kappa\Sigma_k + \lambda\Sigma_l + etc. \quad (30)^7$$

In the subsequent section, “Definition and Properties of Fundamental Equations”, Gibbs developed Massieu’s researches on thermodynamic properties of fluid systems. Gibbs was looking for other “fundamental equations” concerning a thermodynamic system, and involving 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 ψ, χ , and ξ , which he defined starting from ε and the already known equation

⁵ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 64-5.

⁶ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 66.

⁷ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 67-9.

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n \quad (86).$$

He first defined the function

$$\psi = \varepsilon - t\eta \quad (87).$$

By differentiation and comparison with equation (86) we obtain

$$d\psi = -\eta dt - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n \quad (88)$$

He then defined

$$\chi = \varepsilon + pv \quad (89),$$

which through equation (86) became

$$d\chi = t d\eta + v dp + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n \quad (90)$$

Eventually he defined the function

$$\xi = \varepsilon - t\eta + pv \quad (91),$$

which led to

$$d\xi = -\eta dt + v dp + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n \quad (92).''^8$$

⁸ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 87.

The integration of the first fundamental equation (86) led to a finite expression

$$\varepsilon = t\eta - p v + \mu_1 m_1 + \mu_2 m_2 + \dots \mu_n m_n \quad (93).$$

The differentiation of the latter “in the most general manner” led to

$$\begin{aligned} d\varepsilon &= t d\eta + \eta dt - p dv - v dp + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n + m_1 d\mu_1 + m_2 d\mu_2 + \dots m_n d\mu_n \\ d\varepsilon &= (t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n) + \eta dt - v dp + m_1 d\mu_1 + m_2 d\mu_2 + \dots m_n d\mu_n \\ d\varepsilon &= (d\varepsilon) + \eta dt - v dp + m_1 d\mu_1 + m_2 d\mu_2 + \dots m_n d\mu_n \end{aligned}$$

and then to

$$\begin{aligned} 0 &= \eta dt - v dp + m_1 d\mu_1 + m_2 d\mu_2 + \dots m_n d\mu_n \\ v dp &= \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \dots m_n d\mu_n \quad (97, 98). \\ dp &= \frac{\eta}{v} dt + \frac{m_1}{v} d\mu_1 + \frac{m_2}{v} d\mu_2 + \dots \frac{m_n}{v} d\mu_n \end{aligned}$$

This is another fundamental equation, which Gibbs added to the equations already displayed.⁹ Other equations, he noticed, corresponding to other “sets of quantities” might be added.

Under specific conditions, the functions ψ , χ , and ξ assumed specific meanings, and led to new conditions of equilibrium.

“The quantity ψ has been defined for any homogeneous mass by the equation

$$\psi = \varepsilon - t\eta \quad (105).$$

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

$$\psi' - \psi'' = \varepsilon' - \varepsilon'' - t(\eta' - \eta'') \quad (106).$$

⁹ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 87-8.

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

$$\varepsilon' - \varepsilon'' = W - Q \quad (107),$$

and

$$t(\eta'' - \eta') = Q \quad (108).$$

Hence

$$\psi' - \psi'' = W \quad (109);$$

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

$$-d\psi = dW''^{10}$$

In other words, the function ψ is “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”. The system under consideration does not experience purely thermal (calorimetric) transformations. In this case, the function ψ plays the role of the internal energy ε , and the condition of equilibrium becomes

$$(\delta\psi)_t \geq 0 \quad (111).$$

The equivalence between the condition (2) and the condition (111), for a transformation with equal temperature in the initial and final states, was demonstrated by Gibbs in the following passages.

Gibbs showed that the function ξ plays a similar role for transformations maintaining equal temperature and pressure in their initial and final states, so that

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

¹⁰ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 89.

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 can be qualified as “the *heat function for constant pressure*”, and its decrease represents “the heat given out by the system”. The system undergoes a purely thermal transformation, and also in this case Gibbs stressed the analogy with the internal energy ε , which “might be called the heat function for constant volume”.¹¹

Gibbs was weaving a net of mechanic-thermodynamic functions and relationship, in order to plot a more general mechanics. He followed the track of the narrower-scope analytic mechanics, but aimed at a wider-scope mechanics, able to encompass mechanics, thermodynamics and chemistry.

This generalisation led Gibbs to the generalisation of the concept of “potential”. Every term $\mu_1, \mu_2, \dots \mu_n$, among “the differential coefficients of ε taken with respect to $m_1, m_2, \dots m_n$ ”, 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 aspect, independently of the choice of the fundamental function:

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

The subscript letters denote the quantities which remain constant in the differentiation, “ m being written for brevity for all the letters $m_1, m_2, \dots m_n$, except the one occurring in the denominator”. In this way, the fundamental functions ε, ψ, χ , and ζ partake in a sort of symmetry: ε as function of volume and entropy can be replaced by ψ as

¹¹ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89-91.

function of temperature and volume, by χ as function of entropy and pressure, and by ζ as function of temperature and pressure.¹²

Another aspect of the symmetry underlying the fundamental functions was pointed out by Gibbs in the subsequent section “Geometrical Illustrations”. He made reference to his “method ... of representing the thermodynamic properties of substances ... by means of surfaces”. In brief, every fundamental function, associated to its two independent variables, defines a threefold system of co-ordinates, wherein the graph of the corresponding function $z = f(x, y)$ can be drawn. We can define a function $\varepsilon = f_\varepsilon(v, \eta)$ as well as a function $\zeta = f_\zeta(t, p)$.

“Comparing the two methods, we observe that in one

$$v = x, \quad \eta = y, \quad \varepsilon = z, \\ p = -\frac{dz}{dx}, \quad t = \frac{dz}{dy}, \quad \mu = \zeta = z - \frac{dz}{dx}x - \frac{dz}{dy}y;$$

and in the other

$$t = x, \quad p = y, \quad \mu = \zeta = z, \\ \eta = -\frac{dz}{dx}, \quad v = \frac{dz}{dy}, \quad \varepsilon = z - \frac{dz}{dx}x - \frac{dz}{dy}y.$$

Now $\frac{dz}{dx}$ and $\frac{dz}{dy}$ are evidently determined by the inclination of the tangent plane, and $z - \frac{dz}{dx}x - \frac{dz}{dy}y$ is the segment which it cuts off on the axis of Z. The two methods, therefore, have this reciprocal relation, that the quantities represented in one by the position of a point in a surface are represented in the other by a position of a tangent plane.”¹³

We have in front of us a sort of symmetry, which transforms the space (v, η, ε) into the space (t, p, ζ) , and the values of one function into the position of a tangent plane.

¹² Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89 and 93. 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 .”

¹³ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 116.

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” $\frac{dx}{dx'}, \frac{dx}{dy'}, \dots, \frac{dz}{dz'}$ connecting “the *strained* and the *unstrained* states” of the solid.¹⁴ 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. I will not try to reconstruct the whole deduction, but will confine myself only to outlining the main steps.

He labelled r_1 , r_2 , and r_3 “the ratios of elongation for the three principal axes of strain”, and r_0 “the common value of r_1, r_2, r_3 which will make the stress vanish at any given temperature”. Then he wrote the first fundamental equation “for an isotropic solid”, represented “with sufficient accuracy by the formula”

$$\varepsilon_{V'} = i' + e' E + f' F + h' H, \quad (443)$$

where i' , e' , f' , and h' “denote functions of $\eta_{V'}$ ”, whereas E , F , and H are expressions involving the differential coefficients, and are mathematically linked to r_1, r_2, r_3 . The second fundamental equation is

$$\psi_{V'} = i + e E + f F + h H, \quad (444)$$

where i , e , f , and h “denote functions of t ”. Gibbs defined the elasticity of volume and density under the condition of constant temperature, V and R , as

¹⁴ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 184-5.

$$V = -v \left(\frac{dp}{dv} \right)_t \quad r_0 R = \frac{d^2 \psi_{V'}}{\left(d \frac{dx}{dy'} \right)^2}.$$

Whit the help of the relationship

$$p = - \left(\frac{d\psi}{dv} \right)_t,$$

he arrived at

$$V = -\frac{2}{3} \frac{e}{r_0} + \frac{4}{3} f r_0 \quad R = \frac{2e}{r_0} + 2 f r_0.$$

For V' and R' , the elasticity of volume under the condition of constant entropy, he arrived at the similar expression

$$V' = -\frac{2}{3} \frac{e'}{r_0} + \frac{4}{3} f' r_0 \quad R' = \frac{2e'}{r_0} + 2 f' r_0.^{15}$$

Beyond the specific deduction and the specific mathematical steps, it is worth noticing the commitment to a unified mechanic-thermodynamic approach to physical phenomena.

Here we are far from Boltzmann's commitment to reduce macroscopic thermodynamics to a microscopic mechanics involving invisible molecules. Gibbs' conceptual path is, in some way, the reverse of Boltzmann's: if the latter tried to reduce thermodynamics to a molecular dynamics, the former looked upon classic mechanics as a sub-set of a more general thermodynamics-mechanics. Gibbs briefly mentioned

¹⁵ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 209-14.

molecules in the first lines of the short section “On Certain Points relating to the Molecular Constitution of Bodies”. He started from the distinction between “proximate components” and ultimate components, namely “components which would be sufficient to express its ultimate components”, in a body. 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, Gibbs noticed, the number of proximate components “exceeds” the number of ultimate components. He made reference to “other cases”, wherein “we suppose a great number of different sorts of molecules, which differ in composition”. Molecules, proximate components and ultimate components were put on the same level, as different representations of a body made of different components. He went on making reference to “other cases” which “are explained” by molecules: there are “molecules which differ in the quantity of matter which they contain, but not in the kind of matter”, There are also other cases, wherein “there appear to be different sorts of molecules”: they “differ neither in the kind nor in the quantity of matter which they contain, but only in the manner in which they are constituted”. He did not put bodies and their “components” on the one hand, and molecules on the other: he did not look upon the latter as qualitatively different from the former. He did not see the explanations in terms of “components” as qualitatively different from the explanations in terms of “molecules”: all cases “are essentially the same in principle”.¹⁶ This is a very different approach from Boltzmann’s. There is not any gap between a visible, macroscopic level and an invisible, microscopic level, which would represent the *explanation* of the former. Neither tried Gibbs to devise any kind of model with regard to molecules, nor tried to make remark or assumptions on the geometrical or dynamical relationships among hypothetical molecules.

In a subsequent abstract published in the American Journal of Science in 1878, Gibbs did not mention molecules. From the outset he stressed the role of entropy, whose importance, he claimed, “does not appear to have been duly appreciated”. According to

¹⁶ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 138.

Gibbs, “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”. Besides the functions ε and η , and the corresponding condition of equilibrium, the role of the function ψ is stressed. When “we assume that the temperature of the system is uniform”, the condition of equilibrium “may be expressed by the formula”

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

On the one hand, this formula seems to Gibbs suitable for equilibrium in “a purely mechanical system”, as a mechanical system is nothing else but “a thermodynamic system maintained at a constant temperature”. On the other hand, this formula would allow us to realize a conceptual “transition” from “ordinary mechanics” to thermodynamics. In Gibbs view, the functions $-\varepsilon$ and $-\psi$ “may be regarded as a kind of force-function”, namely a generalisation of the concept of mechanical potential. The conditions of equilibrium $(\delta\varepsilon)_\eta \geq 0$ and $(\delta\psi)_t \geq 0$ would represent “extensions of the criterion employed in ordinary statics to the more general case of a thermodynamic system”.¹⁷ This is indeed the keystone of Gibbs theoretical researches collected into the papers published between 1875 and 1878. Mechanics is a part of thermodynamics: thermodynamics plays the role of a generalised mechanics.

As remarked by Truesdell some decades ago, Gibbs built up a remarkable “axiomatic structure”, but he was committed to a sort of generalised Statics rather a generalised Dynamics: his theory was “no longer the theory of motion and heat interacting, no longer thermodynamics, but only the beginnings of thermostatics”.¹⁸

¹⁷ Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 354-5.

¹⁸ Truesdell C. 1984, p. 20. The same concept is re-stated in Truesdell C. 1986, p. 104. Nevertheless Truesdell appreciated Gibbs commitment to give a deep physical meaning to the entropy. 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.”

7. The “free energy” in Physics and Chemistry

After having published many papers on physics and physiology since the middle of the nineteenth century, in 1882 Helmholtz put forward a mathematical theory of heat encompassing physical and chemical phenomena. He was a scientific authority: it is worth stressing that, in the scientific community of the time, he played a role quite different from Massieu, Rankine and Gibbs. His theoretical remarks were not completely original, for he followed the pathway of the mathematisation of Thermodynamics in accordance with the tradition of Analytic Mechanics. Although this pathway had already been undertaken by Massieu and Gibbs, his original contribution dealt with the concept of “free energy”.¹

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 could not be interpreted in terms of mere production or consumption of heat in production or dissolutions of compounds. 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 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 betreffende 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

¹ 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 by 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.

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.²

Confining himself to chemical processes going on by themselves, without any external driving force, Helmholtz tried to go beyond the interpretation of the heat sent out as a measure of “the strength of chemical affinity”. It was not important that a stronger release of heat be accompanied by a stronger affinity, as far as the latter is revealed by the establishment or dissolution of chemical bonds: the two things did not necessarily coincide. The fact is that chemical actions could give birth to “other kinds of energy besides mere heat”, and even in chemical processes the separation between the component corresponding to work and the component corresponding to heat should have been taken into account. He qualified the two kinds of energy as “free and bound energy”.

Helmholtz had found that 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”. According to Clausius’ “universal law”, it was just the amount of the free energy, and not that of the “whole energy”, which decided in what direction affinity operated. The second law allowed Helmholtz to go beyond the unsatisfactory interpretation of chemical processes in terms of heat gained or lost. He tried to weave a unified theoretical net involving thermal, chemical and electrodynamic processes: it was just that complex interplay among different phenomena to have led him to the concept of free energy.

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

² 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.

können. [...] Für die nach festen Aequivalenten geschlossenen chemischen Verbindungen im engeren Sinne dagegen bilden die elektrolytischen Prozesse 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.³

The galvanic cell was indeed the case Helmholtz tried to describe in thermodynamic terms. He reminded the reader that processes taking place in a galvanic cell were “completely reversible”: the development of heat in a closed wire was proportional to the resistance and the squared electric current. In a galvanic cell at uniform temperature ϑ , where an “electric quantum” $d\varepsilon$ passes through, the state can change if a chemical change proportional to $d\varepsilon$ occurs. We look upon the state of the cell as defined by the amount of electricity ε , which has passed through in a given definite direction. If we connect the two ends of the battery to the plates of a high capacity condenser, which is charged at the difference of potential p , then the passage of $d\varepsilon$ from the negative to the positive plate would correspond to the increase $p \cdot d\varepsilon$ in the amount of the available electrostatic energy. Helmholtz labelled dQ the amount of heat which we must supply (or withdraw, if negative) in order to keep constant the temperature ϑ at the passage of $d\varepsilon$. If we label $\mathfrak{J}$ the mechanical equivalent of the unity of heat, and U the total energy, which can be considered as function of ϑ and ε , the law of conservation of energy leads to

$$\mathfrak{J} \cdot dQ = dU + p \cdot d\varepsilon, \quad \text{or} \quad \mathfrak{J} \cdot dQ = dU + dW.$$

In this case, the term qualified as external or macroscopic mechanical work was in reality an electric work. A simple mathematical development allowed Helmholtz to write

³ Helmholtz 1882, p. 960.

$$\mathfrak{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \frac{\partial U}{\partial \varepsilon} \cdot d\varepsilon + p \cdot d\varepsilon,$$

$$\mathfrak{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \left(\frac{\partial U}{\partial \varepsilon} + p \right) \cdot d\varepsilon \quad (1).$$

On the other hand, according to Carnot-Clausius' principle, there was a function of ϑ and ε , which Clausius called the *entropy* of the system, whose variation was

$$dS = \frac{1}{\vartheta} \cdot \mathfrak{J} \cdot dQ = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \frac{1}{\vartheta} \cdot \left(\frac{\partial U}{\partial \varepsilon} + p \right) \cdot d\varepsilon \quad (1a),$$

where

$$\frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \frac{\partial S}{\partial \varepsilon} = \frac{1}{\vartheta} \cdot \left(\frac{\partial U}{\partial \varepsilon} + p \right).^4$$

The following results required more complex mathematical steps. The expression for the second derivative $\partial^2 S / \partial \vartheta \cdot \partial \varepsilon \equiv \partial^2 S / \partial \varepsilon \cdot \partial \vartheta$ could be derived from both of the above equations. From the first, we have

$$\frac{\partial^2 S}{\partial \vartheta \cdot \partial \varepsilon} = \frac{1}{\vartheta} \cdot \frac{\partial^2 U}{\partial \vartheta \cdot \partial \varepsilon}.$$

From the second, we have

$$\frac{\partial^2 S}{\partial \vartheta \cdot \partial \varepsilon} = -\frac{1}{\vartheta^2} \cdot \left(\frac{\partial U}{\partial \varepsilon} + p \right) + \frac{1}{\vartheta} \cdot \left(\frac{\partial^2 U}{\partial \vartheta \cdot \partial \varepsilon} + \frac{\partial p}{\partial \vartheta} \right).$$

When we compare the last two expressions, we find

⁴ Helmholtz 1882, pp. 961-2.

$$\frac{1}{\vartheta} \cdot \frac{\partial^2 U}{\partial \vartheta \cdot \partial \varepsilon} = -\frac{1}{\vartheta^2} \cdot \left(\frac{\partial U}{\partial \varepsilon} + p \right) + \frac{1}{\vartheta} \cdot \frac{\partial^2 U}{\partial \vartheta \cdot \partial \varepsilon} + \frac{1}{\vartheta} \cdot \frac{\partial p}{\partial \vartheta},$$

$$\frac{1}{\vartheta^2} \cdot \left(\frac{\partial U}{\partial \varepsilon} + p \right) = \frac{1}{\vartheta} \cdot \frac{\partial p}{\partial \vartheta},$$

$$\vartheta \cdot \frac{\partial p}{\partial \vartheta} = \frac{\partial U}{\partial \varepsilon} + p.$$

Now we can write the equation (1) as

$$\mathfrak{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \vartheta \cdot \frac{\partial p}{\partial \vartheta} \cdot d\varepsilon \quad (1^*),$$

where the last term corresponded to the mechanical equivalent of heat which we must supply to the galvanic cell, during the passage of $d\varepsilon$, “in order to keep constant the temperature”. Indeed, if we let the variation of temperature $d\vartheta$ vanish, then

$$\vartheta \cdot \frac{\partial p}{\partial \vartheta} \cdot d\varepsilon = \mathfrak{J} \cdot dQ.^5$$

In processes taking place at constant temperature, the combination of the first and second Principles of Thermodynamics allows us to compute the balance between electric and thermal contributions required in order to maintain the thermal equilibrium.

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”. Indeed, in the next section, he arrived at Thermodynamics after a short detour through the “great simplification and generality” reached by Analytic Mechanics or “Dynamics”. He focussed on a key-concept, which could be labelled “potential energy”, “function of force” (*Kräftefunction*), “tension force” (*Quantität der*

⁵ Helmholtz 1882, p. 962.

Spannkräfte), or “Ergal”, and which could be associated to the names of Clausius, C.G.J. Jacobi, and himself. In the first applications of this concept, “variations of temperature had not been taken into account”, mainly because the force and the corresponding work did not depend on the temperature, as in the case of gravitation. In other cases, “the temperature in the course of the processes under investigation could be looked upon as constant”, or as “function of certain mechanical entities”, like gas density in the case of the velocity of sound. The fact is that “some constant physical entities” appearing in the “Ergal”, like density and coefficients of elasticity, “really changed with temperature”. The right mathematical procedure could not stem but “from the two equations of thermodynamics put forward by Clausius”.⁶

Following Clausius pathway, at first Helmholtz confined himself to the simple case of a body whose state depended “only on temperature and on another parameter”. In the more complex case of systems depending on “many other parameters besides temperature”, the procedure was “founded on the same principles”. He labelled ϑ the absolute temperature, and p_α the parameters defining the state of the body: they neither depended on each other nor on temperature. If Clausius could rely on “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. As already shown by Massieu and Gibbs, all thermodynamic properties of a given system could be derived by a single function.

Helmholtz labelled P_α the external forces corresponding to the parameter p_α , and $P_\alpha \cdot dp_\alpha$ the corresponding work. If the total external work was

$$dW = \sum_{\alpha} (P_\alpha \cdot dp_\alpha),$$

the first principle could be written as

⁶ Helmholtz 1882, pp. 965-6.

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

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

Ich nehme zunächst ein beliebig zusammengesetztes System von Massen an, welche alle dieselbe Temperatur ϑ haben und alle auch immer die gleichen Temperaturänderungen erleiden. Der Zustand des Systems sei durch ϑ und eine Anzahl von unabhängigen Parametern p_{α} vollständig bestimmt.

Ich bezeichne, wie Hr. Clausius, die bei einer verschwindend kleinen Aenderung im Zustande des Körpers hinzutretende Wärmemenge mit dQ , die innere Energie mit U . Das Gesetz von der Constanz der Energie erhält dann die Forme

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

Hierin bezeichnet $\mathfrak{J}$ 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.⁷

Beside this generalisation of the first principle, Helmholtz put forward a similar generalisation of the second law. At first he reminded the reader that, in case of reversible closed cycles, the second law stated that

$$\int \frac{dQ}{\vartheta} \cdot d\vartheta = 0.$$

Then he defined the entropy S as

⁷ Helmholtz 1882, pp. 966-7.

$$\frac{1}{\vartheta} \cdot dQ = dS = \frac{\partial S}{\partial \vartheta} \cdot d\vartheta + \sum_{\alpha} \left[\frac{\partial S}{\partial p_{\alpha}} \cdot dp_{\alpha} \right] \quad (1a).$$

From equation (1) we can write

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

and from (1a) it follows that

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

When we compare the right-hand sides of the last two equations, we find

$$\mathfrak{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \mathfrak{J} \cdot \frac{\partial S}{\partial p_{\alpha}} = \frac{1}{\vartheta} \cdot \left(\frac{\partial U}{\partial p_{\alpha}} + P_{\alpha} \right). \quad ^8 \quad [*].$$

The last equation can be written as

$$\mathfrak{J} \cdot \frac{\partial S}{\partial p_{\alpha}} - \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial p_{\alpha}} = \frac{1}{\vartheta} \cdot P_{\alpha} \quad \text{or} \quad P_{\alpha} = \mathfrak{J} \cdot \vartheta \cdot \frac{\partial S}{\partial p_{\alpha}} - \frac{\partial U}{\partial p_{\alpha}}.$$

In the end, Helmholtz arrived at the very meaningful equation

$$P_{\alpha} = \frac{\partial}{\partial p_{\alpha}} \cdot (\mathfrak{J} \cdot \vartheta \cdot S - U) \quad (1b).$$

⁸ Helmholtz 1882, p. 967.

If we put

$$\mathcal{F} = U - \mathfrak{J} \cdot \vartheta \cdot S \quad (1e),$$

equation (1b) transforms into

$$P_{\alpha} = - \frac{\partial \mathcal{F}}{\partial p_{\alpha}} \quad (1f),$$

wherein $\mathcal{F}$ is a definite function of ϑ and p_{α} , just like U and S , apart from “an arbitrary additive constant $\alpha - \beta \cdot \mathfrak{J} \cdot \vartheta$ ”.⁹ According to Helmholtz, the function $\mathcal{F}$ represented the potential energy or the “Ergal”. If we derive equation (1e) with regard to temperature, we obtain

$$\frac{\partial \mathcal{F}}{\partial \vartheta} = \frac{\partial U}{\partial \vartheta} - \mathfrak{J} \cdot S - \mathfrak{J} \cdot \vartheta \cdot \frac{\partial S}{\partial \vartheta}.$$

Making use of equation (*), namely

$$\mathfrak{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta},$$

we find that

$$\frac{\partial \mathcal{F}}{\partial \vartheta} = - \mathfrak{J} \cdot S \quad (1g).$$

Finally, from (1e) and (1g), Helmholtz arrived at

⁹ Helmholtz 1882, p. 968.

$$U = \mathcal{F} - \vartheta \cdot \frac{\partial \mathcal{F}}{\partial \vartheta} \quad (1h)^{10}$$

As I have shown in chapter 4, the last two equations had already been derived by the French engineer Massieu: Helmholtz seemed not aware of Massieu result, which had probably not crossed France borderlines.

From the expressions of the functions U and S in terms of $\mathcal{F}$ derivatives, “another interpretation” of equation (*) emerged. From the derivation of equation (1h), it follows that

$$\frac{\partial U}{\partial \vartheta} = \frac{\partial \mathcal{F}}{\partial \vartheta} - \frac{\partial \mathcal{F}}{\partial \vartheta} - \vartheta \cdot \frac{\partial^2 \mathcal{F}}{\partial \vartheta^2} = -\vartheta \cdot \frac{\partial^2 \mathcal{F}}{\partial \vartheta^2}.$$

From the derivation of equation (1g), it follows that

$$\frac{\partial^2 \mathcal{F}}{\partial \vartheta^2} = -\mathfrak{J} \cdot \frac{\partial S}{\partial \vartheta}.$$

Helmholtz could conclude that

$$\frac{\partial U}{\partial \vartheta} = -\vartheta \cdot \frac{\partial^2 \mathcal{F}}{\partial \vartheta^2} = \mathfrak{J} \cdot \vartheta \cdot \frac{\partial S}{\partial \vartheta}.^{11}$$

In the specific case of constant parameters p_α , equation (1) becomes

$$\mathfrak{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta,$$

¹⁰ Helmholtz 1882, pp. 968-9.

¹¹ Helmholtz 1882, p. 969.

and the quantity $\partial U / \partial \vartheta$ represents “the thermal capacity of the system when the parameters are constant”. Helmholtz labelled Γ this capacity, and expressed it in terms of $\mathcal{F}$ derivatives:

$$\mathfrak{J} \cdot \Gamma = \frac{\partial U}{\partial \vartheta} = -\vartheta \cdot \frac{\partial^2 \mathcal{F}}{\partial \vartheta^2} \quad (1i).$$

Since Γ and ϑ “are necessarily positive quantities”, it follows that $\partial^2 \mathcal{F} / \partial \vartheta^2$ is necessarily negative. Equations (1g) and (1h) suggest that $-\partial \mathcal{F} / \partial \vartheta$ (namely $\mathfrak{J} \cdot S$) and $\mathcal{F} - \vartheta \cdot \partial \mathcal{F} / \partial \vartheta$ (namely U) must increase “in the case of increasing temperature and stationary parameters”.¹²

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

Die Funktion $\mathcal{F}$ fällt, wie wir gesehen haben, für isotherme Veränderungen mit dem Werthe der potentiellen Energie für die unbeschränkt verwandelbaren Arbeitswerthe zusammen. Ich schlage deshalb vor, diese Grösse die freie Energie des Körpersystems zu nennen.

Die Grösse

$$U = \mathcal{F} - \vartheta \cdot \frac{\partial \mathcal{F}}{\partial \vartheta} = \mathcal{F} + \mathfrak{J} \cdot \vartheta \cdot S$$

könnte, wie bisher, als die gesammte (innere) Energie bezeichnet werden; die etwa vorhandene lebendige Kraft der Massen des Systems bleibt von $\mathcal{F}$ wie von U ausgeschlossen, so weit sie zu den frei verwandelbaren Arbeitsäquivalenten gehört, und nicht zu Wärme geworden ist. Dann könnte man die Grösse:

$$U - \mathcal{F} = -\vartheta \cdot \frac{\partial \mathcal{F}}{\partial \vartheta} = \mathfrak{J} \cdot \vartheta \cdot S$$

¹² Helmholtz 1882, p. 969.

als die gebundene Energie bezeichnen.

Vergleicht man den Werth der gebundene Energie:

$$U - \mathcal{F} = \mathfrak{J} \cdot \vartheta \cdot S ,$$

mit der Gleichung (1a):

$$dQ = \vartheta \cdot dS ;$$

so ergibt sich, dass die gebundene 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.¹³

According to Helmholtz, another term should have appeared in the list of the energies: the living force or current energy (“actuelle Energie”). It corresponded specifically to “the living force of the ordered motion”, not to be confused with “the work-equivalent of heat”, which could be considered as “living force of hidden molecular motions”. Not so easy appeared to Helmholtz the distinction between ordered and disordered motions from the mechanical point of view, wherein some kind of spatial correlations were at stake. He only found “good reasons” to assume that thermal motion was of the disordered kind, and that entropy was “a measure of disorder”. The transformations of energy taking place in “living tissues” appeared to Helmholtz even more difficult to tackle, despite they were of particular importance for a scientist who had begun his career as a physiologist.¹⁴

In the second section of his paper, Helmholtz tried to “rephrase the other two quantities dW and dQ which appears in Clausius’ equations”, and for this purpose he found 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 was reserved to a complete variation, wherein the temperature also changed. For a function φ of p_α and ϑ , he wrote

¹³ Helmholtz 1882, p. 971.

¹⁴ Helmholtz 1882, pp. 971-2, footnote included.

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

What he called “freely convertible external work” could be expressed in term of the potential $\mathcal{F}$ when we remember that $P_{\alpha} = -\partial\mathcal{F}/\partial p_{\alpha}$:

$$\begin{aligned} dW &= \sum (P_{\alpha} \cdot dp_{\alpha}) = -\delta\mathcal{F} = \\ & -d\mathcal{F} + \frac{\partial\mathcal{F}}{\partial\vartheta} \cdot d\vartheta = -d\mathcal{F} - \mathfrak{J} \cdot S \cdot d\vartheta \end{aligned} \quad (1m).^{15}$$

According to the new symbols, the first principle, namely equation (1), assumed the form

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

With the help of the expression of U in equation (1h), namely $U = \mathcal{F} - \vartheta \cdot \partial\mathcal{F}/\partial\vartheta$,

$$\mathfrak{J} \cdot dQ = d\mathcal{F} - d\left(\vartheta \cdot \frac{\partial\mathcal{F}}{\partial\vartheta}\right) - \delta\mathcal{F}.$$

$$\text{Since } d\mathcal{F} = \delta\mathcal{F} + \frac{\partial\mathcal{F}}{\partial\vartheta} \delta\vartheta,$$

$$\begin{aligned} \mathfrak{J} \cdot dQ &= \frac{\partial\mathcal{F}}{\partial\vartheta} \cdot d\vartheta - d\left(\vartheta \cdot \frac{\partial\mathcal{F}}{\partial\vartheta}\right) = \frac{\partial\mathcal{F}}{\partial\vartheta} \cdot d\vartheta - \frac{\partial\mathcal{F}}{\partial\vartheta} \cdot d\vartheta - \vartheta \cdot d\left(\frac{\partial\mathcal{F}}{\partial\vartheta}\right) = \\ & -\vartheta \cdot d\left(\frac{\partial\mathcal{F}}{\partial\vartheta}\right) = \vartheta \cdot \mathfrak{J} \cdot dS \end{aligned} \quad (1n),$$

¹⁵ Helmholtz 1882, pp. 972-3.

in accordance with equation (1g). This appeared to Helmholtz an interesting conclusion, for he had found that “the fundamental equations” (1) and (1a), as well as all the “conclusions derived by Clausius and other physicists”, were satisfied “even in the case of more parameters”.¹⁶

Then he tried to specify the concept of “bound energy” or “bound work”, which he labelled G . From the mathematical point of view, the sum of $\mathcal{F}$ and G had to equal the total energy U :

$$\mathcal{F} + G = U \quad (^\circ).$$

From equation (1e), $\mathcal{F} = U - \mathfrak{J} \cdot \vartheta \cdot S$, and the term G could not be different from

$$G = \mathfrak{J} \cdot \vartheta \cdot S.$$

From the computation of its variation,

$$dG = \mathfrak{J} \cdot \vartheta \cdot dS + \mathfrak{J} \cdot S \cdot d\vartheta = \mathfrak{J} \cdot dQ + \mathfrak{J} \cdot S \cdot d\vartheta \quad (^\circ^\circ),$$

Helmholtz found that G grew firstly “at the expense of the entering heat dQ ”, and secondly “at the expense of the free energy” (by $\mathfrak{J} \cdot S \cdot d\vartheta$), when temperature rose.

On the other hand, the variation of $\mathcal{F}$,

$$d\mathcal{F} = \delta\mathcal{F} + \frac{\partial\mathcal{F}}{\partial\vartheta} \cdot d\vartheta = -dW - \mathfrak{J} \cdot S \cdot d\vartheta \quad (^\circ^\circ^\circ),$$

showed that the free energy decreased by that amount $\mathfrak{J} \cdot S \cdot d\vartheta$, and by the amount of external work, in accordance with the equation (1g)

¹⁶ Helmholtz 1882, pp. 972-3.

$$-\frac{\partial \mathcal{F}}{\partial \vartheta} \cdot d\vartheta = \mathfrak{J} \cdot S \cdot d\vartheta. {}^{17}$$

As Helmholtz remarked, when temperature increases, “free energy transforms into bound energy by the specified amount” $\mathfrak{J} \cdot S \cdot d\vartheta$. In particular, in purely “dissipative processes” giving rise to “irreversible transformations”, $dW = 0$; equation (°°) became $d\mathcal{F} = -\mathfrak{J} \cdot S \cdot d\vartheta$, and the complementary equation (°°) yielded $d\mathcal{G} = \mathfrak{J} \cdot dQ - d\mathcal{F}$.

If we invert equations (°°) and (°°°),

$$\mathfrak{J} \cdot dQ = d\mathcal{G} - \mathfrak{J} \cdot S \cdot d\vartheta \quad (^\circ),$$

$$dW = -d\mathcal{F} - \mathfrak{J} \cdot S \cdot d\vartheta \quad (^\circ{}^\circ),$$

we have a mathematical and conceptual alternative to the first principle expressed in terms of W and Q : $\mathcal{F} + \mathcal{G} = U$ instead of $\mathfrak{J} \cdot dQ = dU + dW$. The new form of equations (°°) and (°°°) allows us to understand Helmholtz statement “all the external work is supplied at the expense of the free energy, and heat at the expense of the bound energy”. Indeed, if dQ' represented the heat sent out by the system, we should invert the signs in (°°), and therefore

$$\mathfrak{J} \cdot dQ' = -d\mathcal{G} + \mathfrak{J} \cdot S \cdot d\vartheta. {}^{18}$$

In the specific case of adiabatic transformations, $dQ = 0$, and therefore $d\mathcal{G} = \mathfrak{J} \cdot S \cdot d\vartheta$. Equation (°°°) becomes $d\mathcal{F} = -dW - d\mathcal{G}$ or

$$dW = -d\mathcal{F} - d\mathcal{G},$$

¹⁷ Helmholtz 1882, p. 975.

¹⁸ Helmholtz 1882, pp. 975-6. Helmholtz theoretical re-interpretation of the first Principle of Thermodynamics can be looked upon as an important stage in the reshaping of chemical thermodynamics, even though A.F. Horstmann and Gibbs had already acknowledged the role of entropy in chemical processes. In France, the influential chemist M. Berthelot went on with relying on the old Thermo-Chemistry. See Kragh H. 1993, pp. 417-8, and 423.

letting Helmholtz conclude that, in this case, “work is produced at the expense of both free and bound energy”. In the same kind of transformations, $dS = 0$, and

$$0 = \mathfrak{J} \cdot dQ = \mathfrak{J} \cdot \vartheta \cdot dS = d(\mathfrak{J} \cdot \vartheta \cdot S) - \mathfrak{J} \cdot S \cdot d\vartheta ,$$

$$0 = dG - \mathfrak{J} \cdot S \cdot d\vartheta = d(U - \mathcal{F}) - \mathfrak{J} \cdot S \cdot d\vartheta ,$$

$$d(U - \mathcal{F}) = \mathfrak{J} \cdot S \cdot d\vartheta .$$

The last equation allows us to decode Helmholtz statement, “the entropy S can be looked upon as the thermal capacity when heat is produced at the expense of the free energy” in adiabatic transformations. Provided that the expression “heat is produced” did not mean the heat exchanged $dQ = 0$, but the *internal* heat or internal energy, the left-hand side of the last equation would correspond to “heat produced at the expense of the free energy”.

In the specific case of isothermal transformations, $d\vartheta = 0$, and equations (°°°) and (°°) become

$$dW = -d\mathcal{F}$$

$$dG = \mathfrak{J} \cdot dQ .$$

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”.¹⁹

In the last short section of the paper, he briefly discussed “the conditions of equilibrium” and “the direction of spontaneous transformations”. The quantity $\delta\mathcal{F}$ was independent of temperature, and he stated that “any positive value of $\delta\mathcal{F}$, 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 “dissociation of

¹⁹ Helmholtz 1882, p. 975.

chemical bonds”. Only when “ $\delta\mathcal{F}$ begins to move from a nil to a negative value”, the phenomenon of dissociation “could take place”.

Apart from some questionable combination of partial temperature-derivatives and differential operators δ , Helmholtz restated the same concept: “the derivative $\partial\mathcal{F}/\partial\vartheta$ can only change by the supply of new heat dQ ”, wherein the “new heat” corresponded to heat coming “from surrounding bodies”, or from the “transformation of freely convertible work”.²⁰

It is worth remarking that, in 1882, Helmholtz put forward a *mechanical* approach to Thermodynamics in accordance with the tradition of Analytic 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. In some way, he tried to give a microscopic explanation of heat, without any recourse to specific mechanical models. This point deserves to be emphasised. In 1884, in the paper “Principien der Statik monocyclischer Systeme”, Helmholtz follow an intermediate pathway, which was neither Boltzmann neither 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. If the energy associated to the former coordinate corresponded to thermal energy, the energy associated to the latter corresponded to the external thermodynamic work.²¹

As I have already pointed out, different *mechanical* theories of heat were on the stage in the last decades of the nineteenth century, and different meaning of the adjective *mechanical* were at stake. This plurality of theories and meanings shows us how interesting the landscape of the contemporary theoretical physics was.

²⁰ Helmholtz 1882, pp. 976-8.

²¹ Buchwald noticed that Helmholtz put forward an analytic 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 researches collected in the sixth volume of his *Vorlesungen über Theoretische Physik*, see Bierhalter G. 1993, pp. 437-42.

SECOND PART

Duhem third pathway

8. Thermodynamics as a new Mechanics

In 1886, the young physicist 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 the achievement of 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 astonishingly new approach to theoretical thermodynamics, and because of the criticism it contained about M. Berthelot chemical theories.¹

In the “Introduction”, he remarked that ordinary mechanics could not solve problems concerning chemical equilibrium. Although he claimed that the nature of those problems was outside the scope of mechanics, they exhibited “several analogies with equilibrium problems in statics”. We find here two meta-theoretical features of Duhem’s early scientific research: the commitment to widen the scope of Mechanics, and, at the same time, the trust in the mathematical structures of Analytic Mechanics. According to Duhem, “*les physiciens*” should have made use of procedures similar to those used by “*les mécaniciens*” in the context of statics.²

Duhem was also committed to bridge the gap between physics and chemistry: this kind of unification led to the building up of a new generalised mechanics. He was looking for structural analogies between this generalized mechanics and principles already developed in the context of rational mechanics, in particular “the principle of virtual velocities and Lagrange’s theorem”. According to his sensitivity to history and historical reconstructions of physics, he briefly marshalled the theoretical contributions to thermodynamics and thermo-chemistry put forward by M. Berthelot, A. Horstmann, and W. Strutt (Lord Rayleigh) in the 1870s. He mentioned, in particular, F. Massieu, who had put forward two “distinctive functions” endowed with a remarkable property: quantities representing “physical and mechanical properties of bodies (specific heat, rate of expansion, bulk modulus, ..)” could be deduced from it. Massieu’s distinctive

¹ As well-known to historians, Duhem’s criticism about Berthelot and G.J. Lippmann’s theories entailed unpleasant consequences: he never managed to be committed to a chair in Paris. For detailed information about the events linked to that dissertation, see Jaki S.L. 1984, pp. 50-2.

² Duhem P. 1886, p. I.

functions involved both energy and entropy, the most meaningful entities in thermodynamics. The first function depended on temperature and volume, and the second on temperature and pressure.³

“Dans le premier cas, si l’on désigne par T la température absolue, par S l’entropie du corps, par U l’énergie interne, le corps admet pour fonction caractéristique la quantité

$$H = TS - U.$$

Dans le second cas, si l’on garde les notations précédents, et si l’on désigne en outre par A l’équivalent calorifique du travail, par v le volume du corps, et par p la pression qu’il supporte, le corps admet pour fonction caractéristique la quantité

$$H' = TS - U - Apv$$
⁴

Duhem remarked that Massieu had made use of the two functions in the context of a theoretical foundation of Thermodynamics, and J.W. Gibbs in the context of thermochemistry. Then he shortly recollected the main steps of Gibbs’ logical pathway, after having listed the two laws of equilibrium, and the two functions

$$\psi = E(U - TS), \quad \zeta = E(U - TS) + pv,$$

similar to Massieu’s functions, which played the role of potentials.⁵ He then remarked that, in 1882, in the context of thermo-chemistry, Helmholtz had put forward “the distinction between two kinds of energy, the free energy ... and the bound energy”. The former could also be transformed into mechanical work, the latter could only be transformed into heat. Helmholtz’s free energy F , Duhem noticed, was nothing else but Gibbs’ function ψ , proportional to Messieu’s “fonction caractéristique” H :

³ Duhem P. 1886, pp. II-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.

⁴ Duhem P. 1886, p. V.

⁵ Duhem P. 1886, p. VI. The coefficient E is nothing else but “l’équivalent mécanique de la chaleur”. The relationship between mechanical equivalent of heat (E) and thermal equivalent of mechanical work (A) is of course $EA = 1$. At this stage, physical remarks and historical reconstructions are tight linked to each others: it is one of the long-lasting hallmarks of Duhem’s scientific practice.

$$F = E(U - TS) = \psi = -EH$$

Although Helmholtz's function F and Gibbs' function ψ were the same entity, Duhem noticed that their applications were quite different: Helmholtz's was interested in the complex interplay among chemical, thermal, and electric effects in Volta's cells, in particular the relationship between the so-called "Voltaic heat" and "chemical heat".

The first chapter of Duhem's 1886 book concerns the relationship between mechanical and thermal properties of a physical-chemical system. His starting point was nothing else but the two principles of thermodynamics: the basic entities were energy and entropy, the two entities which "take part in the expression of thermodynamic potential". Duhem wrote the first principle as

$$(1) \quad dQ + A d \sum \frac{mv^2}{2} = -dU + A d\tau_e,$$

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 "represents the total differential of a function well specified apart from a constant". With regard to the second principle, Duhem reminded the reader of Clausius mathematical and conceptual steps: at first he mentioned the concept of dQ/T as "*unit of transformation* or merely *transformation*", and the corresponding theorem, "*The sum of transformations throughout a close eversible cycle is nought*". Then he mentioned the extension of Clausius' theorem to reversible "transformations different from a closed cycle": the integral

$$\int_0^1 \frac{dQ}{T}$$

between an initial state (0) and a final state (1) “depends only on the initial and final state of the system”. Clausius had widened the scope of the “second principle of the mechanical theory of heat”, including non-reversible closed cycles: “*The algebraic sum of transformations occurring in a non-reversible closed cycle must be positive*”. Subsequently Clausius had further widened the scope of the principle, including the general case of “whatsoever series of non-reversible transformations”. The keystone of this conceptual path appeared to Duhem the concept of “*transformation non compensée*”, which he tried to synthetically explain by some mathematical steps. He took into account the following cycle: a system pass from the initial state (0) to the final state (1) through different steps, at least one of them being non-reversible. Then the system comes back to (0) through a series of reversible (r) steps. At the end of the cycle,

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

From the definition of entropy S , $\int_{(r) 1}^0 \frac{dQ}{T} = S_1 - S_2$, Duhem could write

$$(4) \quad \int_0^1 \frac{dQ}{T} + S_1 - S_2 = N > 0.$$

The quantity N is just what Duhem, following Clausius, called “*la somme des transformations non compensées*”. In the specific case of isothermal transformations, Duhem could write

$$(5) \quad N = \frac{A}{T} \tau.$$

Going on with the generalisation of mechanical analogies, he interpreted τ as “an amount of work which can be naturally qualified as *non-compensated work*”.⁶ From this analogy, he could infer some statements about reversibility and equilibrium.

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

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

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

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

Ces théorèmes rappellent, par leur forme et par leur objet, le principe des vitesses virtuelles. En thermodynamique, le travail non compensé joue, à certains points de vue, le même rôle que le travail en mécanique.”⁷

For systems without any macroscopic living force, equation (1) would become

$$dQ = -dU + A d\tau_e,$$

and, for isothermal transformations, equations (4) and (5) become

⁶ Duhem P. 1886, pp. 3-7. It is worth noticing that the role of the statement about entropy or “transformation”, corresponding to the second principle of thermodynamics, shifted from “theorem” to “principle”. It is also worth noticing that the word “transformation” could assume two different meanings: its general meaning of “change”, and its specific, technical meaning of “entropy”

⁷ Duhem P. 1886, p. 7. In the following passage, Duhem specified the restrictions to be made on those statements: “Remarquons toutefois que le théorème de thermodynamique n’a pas exactement la même portée que le théorème de mécanique. Le principe des vitesses virtuelles indique les conditions nécessaires et suffisantes pour qu’un système soit en équilibre. Le théorème de thermodynamique indique que, dans certaines circonstances, un système demeure nécessairement invariable ; on ne saurait prétendre que le système ne puisse rester invariable que dans ces conditions.” This specification is important in itself, and with regard to Duhem’s subsequent theoretical researches. See chapter 11 of the present dissertation.

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

The last three equations allowed Duhem to give a mathematical expression for the non-compensated work τ :

$$(6) \quad \tau = ET(S_1 - S_0) - E(U_1 - U_0) + \int_0^1 d\tau_e.$$

If we assume that “external forces stem from a potential W ”, the last equation becomes

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

and we can imagine a more general potential Ω corresponding to the non-compensated work τ :

$$(7) \quad \Omega = E(U - TS) + W, \quad \tau = \Omega_0 - \Omega_1. \quad (8)$$

In Duhem’s words, “non-compensated work ... is equal to the opposite of the variation of Ω ” in an isothermal transformation. The analogy between mechanics and thermodynamics suggested Duhem to choose the name “*thermodynamic potential* of the system” for the function Ω .⁸ 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.”

⁸ Duhem P. 1886, pp. 7-8.

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

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

Lorsque le potentiel thermodynamique est minimum, le système est dans un état d'équilibre stable.”⁹

In two specific instances, either constant volume or constant pressure, Duhem's thermodynamic potential had important consequences from the theoretical point of view as well as from the point of view of “applications”. In the first case, $W = 0$, and the potential Ω becomes

$$F = E(U - TS),$$

which is “Helmholtz's free energy” or Gibbs' ψ function. In the second case, $dW = pdv = d(pv)$, and the potential Ω becomes

$$\Phi = E(U - TS) + pv,$$

which is “nothing else but Gibbs' ζ function”.¹⁰

The following section is definitely the most interesting from the point of view of the relationship between Mechanics and Thermodynamics. On the track of F. Massieu, Duhem expressed “all the parameters specifying the physical and mechanical properties of a system” in terms of the partial derivatives of Massieu's H and H' functions, corresponding to Gibbs' ψ and ζ functions, and to Duhem's F and Φ . The function F had to be considered as a function of volume and temperature, whereas the function Φ

⁹ Duhem P. 1886, p. 9.

¹⁰ Duhem P. 1886, pp. 9-10.

had to be considered as a function of pressure and temperature.¹¹ In order to analyse in detail the second function, Duhem took into account a body “in a condition of equilibrium” and the two law of thermodynamics:

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

The first mathematical step consisted in eliminating dQ and expressing S as a function of p and T :

$$\begin{aligned} dS &= \frac{1}{T}(-dQ) = \frac{1}{T}(dU + A p dv) = \frac{1}{T} \left(\frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial p} dp + A p \frac{\partial v}{\partial T} dT + A p \frac{\partial v}{\partial p} dp \right) = \\ &= \frac{1}{T} \left(\frac{\partial U}{\partial T} dT + A p \frac{\partial v}{\partial T} dT \right) + \frac{1}{T} \left(\frac{\partial U}{\partial p} dp + A p \frac{\partial v}{\partial p} dp \right) = \frac{1}{T} \left(\frac{\partial U}{\partial T} + A p \frac{\partial v}{\partial T} \right) dT + \frac{1}{T} \left(\frac{\partial U}{\partial p} + A p \frac{\partial v}{\partial p} \right) dp \end{aligned}$$

In other words,

$$(11) \quad \begin{cases} \frac{\partial S}{\partial T} = \frac{1}{T} \left(\frac{\partial U}{\partial T} + A p \frac{\partial v}{\partial T} \right) \\ \frac{\partial S}{\partial p} = \frac{1}{T} \left(\frac{\partial U}{\partial p} + A p \frac{\partial v}{\partial p} \right) \end{cases} .^{12}$$

The second mathematical step consisted in taking into account the derivatives of the potential Φ with regard p and T :

$$d\Phi = E dU - E T dS - E S dT + p dv + v dp ,$$

$$\begin{cases} \frac{\partial \Phi}{\partial T} = E \frac{\partial U}{\partial T} - E T \frac{\partial S}{\partial T} - E S + p \frac{\partial v}{\partial T} \\ \frac{\partial \Phi}{\partial p} = E \frac{\partial U}{\partial p} - E T \frac{\partial S}{\partial p} + p \frac{\partial v}{\partial p} + v \end{cases}$$

¹¹ Duhem P. 1886, p. 10.

¹² Duhem P. 1886, p. 11. There are some misprints in the text.

From the comparison between the last equations and equations (11), and from $EA = 1$, it follows that

$$\begin{cases} \frac{\partial \Phi}{\partial T} = E \frac{\partial U}{\partial T} - ET \frac{1}{T} \left(\frac{\partial U}{\partial T} + Ap \frac{\partial v}{\partial T} \right) - ES + p \frac{\partial v}{\partial T} = E \frac{\partial U}{\partial T} - E \frac{\partial U}{\partial T} + EAp \frac{\partial v}{\partial T} - ES + p \frac{\partial v}{\partial T} \\ \frac{\partial \Phi}{\partial p} = E \frac{\partial U}{\partial p} - ET \frac{1}{T} \left(\frac{\partial U}{\partial p} + Ap \frac{\partial v}{\partial p} \right) + p \frac{\partial v}{\partial p} + v = E \frac{\partial U}{\partial p} - E \frac{\partial U}{\partial p} + EAp \frac{\partial v}{\partial p} + p \frac{\partial v}{\partial p} + v \end{cases}$$

In brief,

$$(12) \quad \frac{\partial \Phi}{\partial T} = -ES \quad \text{and} \quad (13) \quad \frac{\partial \Phi}{\partial p} = v.$$

Entropy and volume could be expressed as derivative of the potential Φ , and this result allowed Duhem to undertake the third step: the deduction of some mechanical and thermal properties of the system. He introduced “the coefficient α of dilatation under constant pressure” and “the coefficient ε of compressibility”. From the mathematical point of view,

$$(*) \quad \alpha = \frac{1}{v} \frac{\partial v}{\partial T} \quad \text{and} \quad \varepsilon = -\frac{1}{v} \frac{\partial v}{\partial p}.$$

From equation (13), $\frac{\partial v}{\partial T} = \frac{\partial}{\partial T} \frac{\partial \Phi}{\partial p}$ and $\frac{\partial v}{\partial p} = \frac{\partial^2 \Phi}{\partial p^2}$, and therefore

$$(14) \quad \alpha = \frac{\frac{\partial^2 \Phi}{\partial p \partial T}}{\frac{\partial \Phi}{\partial p}} \quad \text{and} \quad (15) \quad \varepsilon = \frac{\frac{\partial^2 \Phi}{\partial p^2}}{\frac{\partial \Phi}{\partial p}}.$$

The coefficient making reference to “the coefficient α' of dilatation under constant volume” was deduced as well. If

$$\alpha' = \frac{1}{p} \frac{\partial p}{\partial T},$$

we need an expression for $\partial p / \partial T$ in term of the above derivatives. This can be done in the following way: from equations (*),

$$\frac{\partial v}{\partial T} = \alpha v \quad \text{and} \quad \frac{\partial p}{\partial v} = -\frac{1}{\varepsilon v},$$

while $\left| \frac{\partial p}{\partial T} \right| = \left| \frac{\partial p}{\partial v} \frac{\partial v}{\partial T} \right|$ and then $\frac{\partial p}{\partial T} = -\frac{\partial p}{\partial v} \frac{\partial v}{\partial T}$.¹³ Inserting $\partial v / \partial T$ and $\partial p / \partial v$ in the latter,

$$\alpha' = \frac{1}{p} \frac{\partial p}{\partial T} = -\frac{1}{p} \frac{\partial p}{\partial v} \frac{\partial v}{\partial T} = -\frac{1}{p} \left(-\frac{1}{\varepsilon v} \right) (\alpha v) = \frac{\alpha}{\varepsilon} = \frac{\frac{\partial^2 \Phi}{\partial p \partial T}}{\frac{\partial^2 \Phi}{\partial p^2}}.$$

Specific heats were also deduced by Duhem in the same way. Specific heat at constant pressure is nothing else but

$$C = \frac{dQ}{dT} = \frac{\partial U}{\partial T} + A p \frac{\partial v}{\partial T}.$$

In this case, we must express the function U in terms of the potential Φ . This can be done resorting to equation (12) and (13), which offer

¹³ The fact is that $p = p(T)$ and $v = v(T)$ are growing functions whereas $p = p(v)$ is a decreasing function. If the former have positive derivative, the latter has a negative derivative.

¹⁴ Duhem P. 1886, pp. 11-12.

$$S = -\frac{1}{E} \frac{\partial \Phi}{\partial T} \quad \text{and} \quad v = \frac{\partial \Phi}{\partial p}.$$

After having inserted them into the equation which define the potential Φ , Duhem was able to achieve the expression for C . I am showing in detail all the first mathematical steps.

$$(18) \quad \Phi = EU - ETS + pv = EU - ET \left(-\frac{1}{E} \frac{\partial \Phi}{\partial T} \right) + p \frac{\partial \Phi}{\partial p} = EU - T \frac{\partial \Phi}{\partial T} + p \frac{\partial \Phi}{\partial p}.$$

Therefore

$$U = \frac{1}{E} \left(\Phi - T \frac{\partial \Phi}{\partial T} - p \frac{\partial \Phi}{\partial p} \right) \text{ and}$$

$$\frac{\partial U}{\partial T} = A \left(\frac{\partial \Phi}{\partial T} - \frac{\partial \Phi}{\partial T} - T \frac{\partial^2 \Phi}{\partial T^2} - p \frac{\partial^2 \Phi}{\partial T \partial p} \right) = A \left(-T \frac{\partial^2 \Phi}{\partial T^2} - p \frac{\partial^2 \Phi}{\partial T \partial p} \right).$$

At the end, even C could also be expressed in terms of the derivatives of the potential Φ :

$$(19) \quad C = \frac{\partial U}{\partial T} + Ap \frac{\partial v}{\partial T} = A \left(-T \frac{\partial^2 \Phi}{\partial T^2} - p \frac{\partial^2 \Phi}{\partial T \partial p} \right) + Ap \frac{\partial}{\partial T} \frac{\partial \Phi}{\partial p} = -AT \frac{\partial^2 \Phi}{\partial T^2}.^{15}$$

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 connaitre dans l’étude thermique d’un corps peuvent s’exprimer au moyen de Φ et de ses dérivées premières et

¹⁵ Duhem P. 1886, pp. 12-13.

secondes par rapport à la pression et à la température, purvu que l'on suppose le corps placé dans un état d'équilibre."¹⁶

As already remarked, also the potential function F , together with its first and second derivatives with regard to v and T , could be as suitable as Φ in order to express the above coefficients.¹⁷

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*, at Paris faculty of Science. He was awarded "*Docteur en Sciences Mathématiques*" by a authoritative academic board: the president was the mathematician G Darboux, and the examiners were H. Poincaré, then professor of probability calculus and mathematical physics, and E. Bouty, professor of physics. It is worth mentioning 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.¹⁸

Since the "Introduction" he 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 G. Kirchhoff had subsequently tried to overcome those difficulties, but they had merely assumed, at the outset, Poisson's equations, without any attempt at deriving the equations from "more general theories" or at least some "empirical law". According to Duhem, both theoretical and experimental flaws threatened the logical and physical

¹⁶ Duhem P. 1886, p. 13.

¹⁷ See Duhem P. 1886, 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."

¹⁸ 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 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.

foundations of the received magnetic theories. He would have founded his theory on the “unquestioned laws” ruling the interactions between magnets, and on the as much “unquestioned principles” ruling thermodynamics.¹⁹

The first chapter, “Potentiel thermodynamique d’un système qui renferme des aimantes”, was opened by a very general section dealing with “Quelques propositions de Thermodynamique”. If dQ is the heat given out in a “basic transformation”, $d\tau_e$ the work done by “external forces”, T the absolute temperature of all elements of the physical system “when the transformation takes place”, U the internal energy, and S the entropy, once again the “simple” and fundamental laws of Thermodynamics could be write down as

$$dQ = -dU + A d\tau_e \quad \text{and} \quad \frac{dQ}{T} = -dS + A dN.$$

The term A was nothing else but “the thermal equivalent of work”, and dN represented “an infinitely small quantity”, always positive apart from the case of a “reversible” transformation: in such a case the term vanished. It was the term Duhem had already called “*transformation non compensée*”.²⁰

He credited Clausius with having shaped the two propositions expressing “the equivalence between heat and work” and “Carnot’s principle”, and credited Gibbs with having drawn “an almost immediate consequence”, whose “fruitfulness” seemed to Duhem more and more evident. If we introduce a function τ , which gets the properties of energy or work, and is linked to the function N by the relation $dN = d\tau/T$, we can rephrase the two laws of Thermodynamics in order to put τ in prominence. That term was named “*travail non compensé*”, or better “*the uncompensated work accomplished in the course of a isothermal transformation*”. If $E=1/A$, then

$$\frac{dQ}{T} + dS = A dN, \quad \frac{1}{A} \left(\frac{dQ}{T} + dS \right) = \frac{d\tau}{T},$$

¹⁹ Duhem 1888, p. 1.

²⁰ See Duhem 1888, p. 3.

$$d\tau = E(dQ + T dS), \quad d\tau = E(-dU + A d\tau_e + T dS),$$

$$d\tau = -E(dU - T dS) + d\tau_e, \quad \text{and} \quad d\tau = -E d(U - TS) + d\tau_e,$$

being the last step consistent with the choice of isothermal transformations. In the case of external forces stemming from a potential W ,

$$d\tau_e = -dW, \quad d\tau = -E d(U - TS) - dW,$$

$$d\tau = -d[E(U - TS) + W], \quad \text{and} \quad d\tau = -d\Omega,$$

wherein Ω was the potential or the function “of state” he had introduced in 1886.²¹

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 changée 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.”*²²

According to a theoretical approach which borrowed names, concepts and procedures from analytic 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”. The well-known tradition of analytic mechanics

²¹ Duhem 1888, pp. 3-4.

²² Duhem 1888, p. 4.

became a specific instance of a more general mechanics, wherein temperature and “chemical state” were as important as pure mechanical quantities. The usual physical quantities, like shape, position and velocities, could account for the displacement of a physical system, but could not account for its transformations or “change of state”.

“Pour connaître complètement l’état du système, il faudra connaître la position de l’origine de chacun de ces systèmes d’axes et l’orientation des axes. En général, il faut aussi connaître un certain nombre d’autres quantités : forme e volume, état physique et chimique dans lequel il se trouve, température qu’il possède en ses divers points, etc. Lorsque les premières quantités varierons 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.*”²³

According to Duhem, when a physical system did not change its “state”, an infinitesimal displacement could however change the quantity $E(U-TS)$, which he called “internal thermodynamic potential” or τ_i . The work done by “the internal mechanical actions” of a system undergoing no change of “state” corresponded to the change of that potential with the negative sign. The uncompensated work became the sum of two different terms: internal work and external work, according to the relation $d\tau = d\tau_i + d\tau_e$.²⁴

Once again Duhem pointed out the intimate connection he was trying to establish between “rational Mechanics and Thermodynamics”: the latter required an analytic approach. Only in this way Thermodynamics could succeed where ordinary mechanics failed, namely when “a change of state is associated to a displacement”. The key-entity in that re-interpretation of Thermodynamics was “the uncompensated work”, a quantity and a concept which “would be vain to look for” in ordinary mechanics. Duhem specified that the “internal potential” could not be identified with the “internal energy” U , apart from the very particular case of “displacement without change of state”. In general, namely for transformation involving both displacements and changes of state,

²³ Duhem 1888, p. 5.

²⁴ Duhem 1888, pp. 5-6 and 8.

the internal potential was the suitable physical quantity for representing the conditions of equilibrium of a system.²⁵

Consistently with specified the strong conceptual link “tying Mechanics to Thermodynamics”, Duhem tried to deduce the Principle of virtual velocities from “the fundamental principle of Thermodynamics”. In general, he wrote, from the thermodynamic point of view, a physical system “is definitely in stable equilibrium” when, in isothermal transformations, “the uncompensated work ... $-E \delta(U - TS) + \delta\tau_e$ is negative or vanishes”. If the external forces derived from a potential W , the stable equilibrium would be assured when the “thermodynamic potential $\Omega = E(U - TS) + W$ is minimum at the given temperature”. In the specific case of “rational Mechanics”, the 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.”

The last statement, Duhem noted, is nothing else but the criterion of stability put forward by Lagrange, even though “a slight difference” was at stake. That difference dealt with a typical feature of Thermodynamics, which deeply differentiate Thermodynamics from Mechanics: the key-point was equilibrium, in particular necessary and sufficient conditions for equilibrium. As Duhem remarked, in pure Mechanics the principle of virtual velocities is both necessary and sufficient condition for mechanical equilibrium. On the contrary, in Thermodynamics, the second Principle is a sufficient but not necessary condition for equilibrium. A physical system cannot experience “a change of state contrary to Carnot-Clausius’ principle”: if the virtual

²⁵ Duhem 1888, pp. 10-11.

transformations of the system “opposed that principle, the system would be inevitably in equilibrium”. Nevertheless, if the system “can experience a virtual transformation consistent with that principle, we do not know whether that transformation will really take place or not”.²⁶

The most interesting consequence of that subtle difference was the possibility of widening the scope of ordinary mechanics. Even in “mechanical”, but not *purely* mechanical systems, equilibrium could persist when the principle of virtual velocities, as assumed in rational Mechanics, is 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.”²⁷

In the subsequent years, Duhem would have developed the structural analogy between Mechanics and Thermodynamics. At the same time, he would have further widened the scope of the mathematical structures stemmed from the tradition of Analytic Mechanics, by means of concept and laws stemmed from Thermodynamics. In the last years of the 1880s, he began to specify his theoretical pathway: a very general theory, based on the two principle of Thermodynamics, and translated into the language of Analytic Mechanics, by means of differential equations more general than Lagrange’s.

²⁶ Duhem 1888, pp. 12-13.

²⁷ Duhem 1888, p. 13.

9. The “general equations”

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”. 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 done “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 managed to show that Massieu’s functions “could play the role of potentials in the determination of the states of equilibrium” in a given system. If Helmholtz had put forward “similar ideas”, Oettingen had given “an exposition of Thermodynamics of remarkable generality”. Duhem did not claim 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”.¹

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 $\alpha, \beta, \dots, \lambda$. He then introduced some “external forces”, depending on $\alpha, \beta, \dots, \lambda$ and ϑ , and holding the system in equilibrium. Such forces should perform a virtual work

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

A set of $n+1$ equations would correspond to the condition of equilibrium of the physical system:

¹ Duhem 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 Duhem theoretical context it is clear that the expression “mechanical Theory of heat” cannot be interpreted in the sense of Maxwell and Boltzmann. I will discuss briefly the question at the end of the present chapter.

$$\left\{ \begin{array}{l} A = f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta) \\ B = f_\beta(\alpha, \beta, \dots, \lambda, \vartheta) \\ \dots \dots \\ L = f_\lambda(\alpha, \beta, \dots, \lambda, \vartheta) \\ \Theta = f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta) \end{array} \right. \quad ^2$$

From the thermodynamic point of view, every infinitesimal transformation involving the generalized *displacements* $\delta\alpha, \delta\beta, \dots, \delta\lambda$ and $\delta\vartheta$, obeys to the first law

$$dQ = -dU + \frac{1}{E} d\tau_e,$$

which becomes

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

Duhem rewrote the last equation as

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

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

wherein

² Duhem 1891, pp. 233-4.

$$(2) \left\{ \begin{array}{l} R_{\alpha} = \frac{\partial U}{\partial \alpha} - \frac{A}{E} \\ R_{\beta} = \frac{\partial U}{\partial \beta} - \frac{B}{E} \\ \dots\dots\dots \\ R_{\lambda} = \frac{\partial U}{\partial \lambda} - \frac{L}{E} \\ R_{\vartheta} = \frac{\partial U}{\partial \vartheta} - \frac{\Theta}{E} \end{array} \right. .^3$$

The new alliance between Mechanics and Thermodynamics led to a re-interpretation of dQ : heat became some kind of *generalized* work, or the sum of all kinds of *work*, mechanical as well thermal. In Duhem’s hands, the new alliance led to a sort of symmetry between thermal and mechanical quantities. The Lagrangian parameters α , β , ..., λ , and the temperature ϑ , played the same role, and the $n+1$ functions

$$R_{\alpha}, R_{\beta}, \dots, R_{\lambda}, R_{\vartheta}$$

played the role of *generalized thermal capacities*. In order to display those functions in a way closer to thermodynamic lexical habits, Duhem wrote the above series as

$$R_{\alpha}, R_{\beta}, \dots, R_{\lambda}, C,$$

wherein the last term C was nothing else but the ordinary thermal capacity: in some way, the latter typographical choice re-established the pre-previous asymmetry.⁴

At this stage of Duhem’s scientific design, we find a double interpretation of the functions R_{α} , R_{β} , ..., R_{λ} , and R_{ϑ} . According to the mechanical interpretation, at least from the point of view of analytic or *rational* Mechanics, they are generalized forces. According to the thermal interpretation, they are generalized *thermal* capacities. The double interpretation allows us to look upon the two terms in the right side of the

³ Duhem 1891, p. 234.

⁴ Duhem 1891, p. 234.

equation expressing the first principle, $dQ = -dU + (1/E)d\tau_e$, as quantities of the same nature. From the mechanical point of view, they are both generalized works; from the thermal point of view, they are both different *kinds* of heat. It must be stressed that the mechanical interpretation of the term dU is a macroscopic interpretation, far from the mechanical interpretation in terms of microscopic molecular motions, which makes sense in the context of the kinetic theory of heat.

Duhem's mathematical and conceptual rephrasing of Thermodynamics let both symmetries and asymmetries between mechanical and thermal interpretations unfold. He associated the functions R_α , R_β , ..., R_λ , and C to the unifying label "*thermal coefficients of the system*", even though one among them, C , had "specific properties", and deserved the specific label "thermal capacity of the system of variables α , β , ..., λ , and ϑ ".⁵

In the following pages Duhem inquired into the connection between the mathematical and the physical sides of the principle of equivalence. He started from some derivatives of the functions R_α , R_β , ..., R_λ , and R_ϑ . From the equations (2),

$$\begin{aligned}\frac{\partial R_\alpha}{\partial \beta} - \frac{\partial R_\beta}{\partial \alpha} &= \frac{\partial}{\partial \beta} \frac{\partial U}{\partial \alpha} - \frac{1}{E} \frac{\partial A}{\partial \beta} - \left(\frac{\partial}{\partial \alpha} \frac{\partial U}{\partial \beta} - \frac{1}{E} \frac{\partial B}{\partial \alpha} \right) = \frac{\partial}{\partial \beta} \frac{\partial U}{\partial \alpha} - \frac{\partial}{\partial \alpha} \frac{\partial U}{\partial \beta} - \frac{1}{E} \frac{\partial A}{\partial \beta} + \frac{1}{E} \frac{\partial B}{\partial \alpha} \\ \frac{\partial R_\alpha}{\partial \vartheta} - \frac{\partial C}{\partial \alpha} &= \frac{\partial}{\partial \vartheta} \frac{\partial U}{\partial \alpha} - \frac{1}{E} \frac{\partial A}{\partial \vartheta} - \left(\frac{\partial}{\partial \alpha} \frac{\partial U}{\partial \vartheta} - \frac{1}{E} \frac{\partial \Theta}{\partial \alpha} \right) = \frac{\partial}{\partial \vartheta} \frac{\partial U}{\partial \alpha} - \frac{\partial}{\partial \alpha} \frac{\partial U}{\partial \vartheta} - \frac{1}{E} \frac{\partial A}{\partial \vartheta} + \frac{1}{E} \frac{\partial \Theta}{\partial \alpha}\end{aligned}$$

Because of the mathematical features of the function U ,

$$(3) \quad \frac{\partial R_\alpha}{\partial \beta} - \frac{\partial R_\beta}{\partial \alpha} = -\frac{1}{E} \left(\frac{\partial A}{\partial \beta} - \frac{\partial B}{\partial \alpha} \right)$$

$$(3') \quad \frac{\partial R_\alpha}{\partial \vartheta} - \frac{\partial C}{\partial \alpha} = -\frac{1}{E} \left(\frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right)$$

The last equations can be looked upon as the mathematical consequences of the principle of equivalence, or first principle of Thermodynamics. The physical

⁵ Duhem 1891, pp. 234-5.

equivalence between work and heat was transformed into a mathematical *equivalence* between their differential coefficients.

Conversely, we could start from the two sets of $n+1$ functions $A, B, \dots, L, \Theta$, and $R_\alpha, R_\beta, \dots, R_\lambda, C$. If they are the differential coefficients of the virtual work,

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

and of the emitted heat,

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

then equations (3) express a sort of mathematical *equivalence*. The differential expressions dQ and $d\tau_e$ are equal for less than “a uniform function of $\alpha, \beta, \dots, \lambda$, and ϑ , so that

$$E(dQ + dU) = d\tau_e$$

From the physical point of view, the differential expressions dQ and $d\tau_e$ “will be subjected to the principle of equivalence between work and heat”.⁶

Another set of equations showed to be useful in the building up of Duhem’s Thermodynamics. The Lagrangian parameter ϑ could be chosen with no restriction: it should not have been necessarily identified with the absolute temperature. In general, the absolute temperature will be a given function $F(\vartheta)$ of ϑ . This means that the function entropy, a “uniform, finite, and continuous function of $\alpha, \beta, \dots, \lambda$, and ϑ ”, had to be defined as

⁶ Duhem 1891, p. 235.

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

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

This equation can be written separately for every differential coefficient:

$$(4) \quad \left\{ \begin{array}{l} \frac{R_\alpha}{F(\vartheta)} = -\frac{\partial S}{\partial \alpha} \\ \frac{R_\beta}{F(\vartheta)} = -\frac{\partial S}{\partial \beta} \\ \dots\dots\dots \\ \frac{R_\lambda}{F(\vartheta)} = -\frac{\partial S}{\partial \lambda} \\ \frac{R_\vartheta}{F(\vartheta)} = -\frac{\partial S}{\partial \vartheta} \end{array} \right.$$

The mathematical feature of the differential form dS corresponds to the vanishing of its crossed derivatives. In fact,

$$\frac{\partial}{\partial \beta} \frac{R_\alpha}{F(\vartheta)} = -\frac{\partial}{\partial \beta} \frac{\partial S}{\partial \alpha}$$

$$\frac{\partial}{\partial \alpha} \frac{R_\beta}{F(\vartheta)} = -\frac{\partial}{\partial \alpha} \frac{\partial S}{\partial \beta}$$

In other words,

$$(5) \quad \frac{\partial}{\partial \beta} \frac{R_\alpha}{F(\vartheta)} = \frac{\partial}{\partial \alpha} \frac{R_\beta}{F(\vartheta)}, \quad \frac{\partial}{\partial \beta} \frac{R_\alpha}{F(\vartheta)} - \frac{\partial}{\partial \alpha} \frac{R_\beta}{F(\vartheta)} = 0,$$

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

If we take into account the parameters α and ϑ instead of α and β , the resulting equation will be more complicated, since $F(\vartheta)$ is sensitive to the derivation with regard ϑ :

$$(5') \quad \frac{1}{F(\vartheta)} \left(\frac{\partial R_\alpha}{\partial \vartheta} - \frac{F'(\vartheta)}{F(\vartheta)} R_\alpha \right) = \frac{1}{F(\vartheta)} \frac{\partial C}{\partial \alpha}.$$

Also in this case, we could reverse all mathematical and physical steps. If we start from the differential form dQ and the equations (5), then “a uniform function S of the state of the system” must exist, and its form is

$$dS = \frac{dQ}{F(\vartheta)}.$$

According to Duhem, from the physical point of view, that system “satisfies Carnot’s principle”.

As a summary of the complex interplay between mathematics and physics, I quote the passage:

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

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

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

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

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

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

⁷ Duhem 1891, pp. 235-6. The asymmetry between *mechanical* and *thermal* parameters emerges once again.

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

*soient deux différentiels totales.*⁸

Equations (3) and (5) had an even more important consequence from both the mathematical and physical points of view. In fact, they led to a series of equations of the kind

$$(6) \quad \frac{\partial A}{\partial \beta} - \frac{\partial B}{\partial \alpha} = 0.$$

As Duhem remarked, equation (6) says that the $n+1$ functions $f_\alpha, f_\beta, \dots, f_\lambda$, and f_ϑ , which define the differential coefficients $A, B, \dots, L$, and Θ , “could not be chosen arbitrarily”. Moreover equation (6) says that “a uniform, finite, and continue function $\mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta)$ of $n+1$ parameters $\alpha, \beta, \dots, \lambda$, and ϑ there exist”. In terms of vector calculus, if $\mathbf{K} = (A, B, \dots, L)$ and $\nabla \times \mathbf{K} = 0$, according to equation (6), then $\mathbf{K} = \nabla \mathcal{F}$, just because $\nabla \times \nabla \mathcal{F} = 0$ for every $\mathcal{F}$. The gradient of $\mathcal{F}$ can be written component by component, taking care of the specific behaviour of the component Θ , which is “independent of the function $\mathcal{F}$ ”, because of difference between the equation (5') and (5):

$$(7) \quad \left\{ \begin{array}{l} A = \frac{\partial}{\partial \alpha} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \\ B = \frac{\partial}{\partial \beta} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \\ \dots \quad \dots \quad \dots \\ L = \frac{\partial}{\partial \lambda} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \\ \Theta = f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta) \end{array} \right. .^9$$

⁸ Duhem 1891, p. 236. Duhem acknowledged that his mathematical and physical approach had already been outlined by Clausius, Kirchhoff, and Reech in the 1850s and 1860s. See *Ibidem*, p. 237.

⁹ Duhem 1891, pp. 237-8.

From the equations (3') and (5') another interesting outcome could be drawn. Starting from (5'), we have

$$\left(\frac{\partial R_\alpha}{\partial \vartheta} - \frac{\partial C}{\partial \alpha} \right) = \frac{F'(\vartheta)}{F(\vartheta)} R_\alpha;$$

then (3') yields

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

Component by component, Duhem expressed “all the thermal coefficients of the system, apart from the thermal capacity”, in terms of “the equations of equilibrium of the system”, namely $A, B, \dots, L$, and Θ :

$$(8) \quad \left\{ \begin{array}{l} R_\alpha = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \alpha} - \frac{\partial A}{\partial \vartheta} \right) \\ R_\beta = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \beta} - \frac{\partial B}{\partial \vartheta} \right) \\ \dots\dots \\ R_\lambda = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \lambda} - \frac{\partial L}{\partial \vartheta} \right) \end{array} \right.$$

What about the function $R_\vartheta = C$, which could not be derived by the same procedure? The fact is that equation (3'), together with its similar equations, and equations (8) allow us to compute the derivatives of C . Duhem first step consisted of redrafting the equations of the kind (3'):

$$\left\{ \begin{array}{l} \frac{\partial C}{\partial \alpha} = \frac{\partial R_\alpha}{\partial \vartheta} + \frac{1}{E} \left(\frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right) \\ \frac{\partial C}{\partial \beta} = \frac{\partial R_\beta}{\partial \vartheta} + \frac{1}{E} \left(\frac{\partial B}{\partial \vartheta} - \frac{\partial \Theta}{\partial \beta} \right) \\ \dots \dots \\ \frac{\partial C}{\partial \lambda} = \frac{\partial R_\lambda}{\partial \vartheta} + \frac{1}{E} \left(\frac{\partial L}{\partial \vartheta} - \frac{\partial \Theta}{\partial \lambda} \right) \end{array} \right.$$

The second step required the derivatives of the functions R_α , R_β , ..., R_λ , and led to quite complicated expressions for the derivatives of C :

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

The last set of equations shows how deeply entangled were *thermal* and *mechanical* properties of a physical system. The knowledge of “equilibrium equations of a system” allowed Duhem to compute the partial derivatives of the thermal capacity with regard to all the parameters which described the state of the system, “apart from its derivative with regard to temperature”. The thermal capacity were therefore known “except for an unspecified function of temperature”.¹⁰

The complex net of equations developed by Duhem could be simplified by an appropriate choice of the Lagrangian parameters, in accordance with a well-known analytic procedure. In particular, if we choose the absolute temperature as thermal parameter, namely $\vartheta = T$, then $F(T) = T$, and the last set of equations let simpler expressions for C derivatives emerge:

¹⁰ Duhem 1891, pp. 238-9.

$$(11) \left\{ \begin{array}{l} \frac{\partial C}{\partial \alpha} = \frac{T}{E} \left(\frac{\partial^2 \Theta}{\partial \alpha \partial \vartheta} - \frac{\partial^2 A}{\partial \vartheta^2} \right) \\ \frac{\partial C}{\partial \beta} = \frac{T}{E} \left(\frac{\partial^2 \Theta}{\partial \beta \partial \vartheta} - \frac{\partial^2 B}{\partial \vartheta^2} \right) \\ \dots \dots \\ \frac{\partial C}{\partial \lambda} = \frac{T}{E} \left(\frac{\partial^2 \Theta}{\partial \lambda \partial \vartheta} - \frac{\partial^2 L}{\partial \vartheta^2} \right) \end{array} \right.$$

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”: Duhem realised a sort of split between thermal and mechanical features of the system. The corresponding mathematical condition $\Theta = 0$ transformed equations (8) and (9) into “very simple equations”:

$$(14) \left\{ \begin{array}{l} R_\alpha = -\frac{T}{E} \frac{\partial A}{\partial T} \\ R_\beta = -\frac{T}{E} \frac{\partial B}{\partial T} \\ \dots \dots \\ R_\lambda = -\frac{T}{E} \frac{\partial L}{\partial T} \end{array} \right. \quad \text{and} \quad (15) \left\{ \begin{array}{l} \frac{\partial C}{\partial \alpha} = -\frac{T}{E} \frac{\partial^2 A}{\partial T^2} \\ \frac{\partial C}{\partial \beta} = -\frac{T}{E} \frac{\partial^2 B}{\partial T^2} \\ \dots \dots \\ \frac{\partial C}{\partial \lambda} = -\frac{T}{E} \frac{\partial^2 L}{\partial T^2} \end{array} \right. .^{11}$$

In the last system of equations, the existence of mathematical links between the *mechanical* derivatives of the *thermal* scalar C and the *thermal* derivatives of the *mechanical* vector $(A, B, \dots, L)$ shows us the persistence of the deep connection between mechanical and thermal effects, even when we break the formal symmetry between them.

In the third section, “Du potentiel thermodynamique”, Duhem took newly into account the “uncompensated work” and thermodynamic potentials: unfortunately, a

¹¹ Duhem, pp. 239-41.

different mathematical notation with regard his 1888 dissertations makes the equations a bit puzzling. Nevertheless, at the end of the fourth section, Duhem rephrased his 1886 and 1888 equations in a consistent way. He wrote the “*transformation non compensée*” as

$$P = \int_{(1)}^{(2)} \frac{1}{F(\vartheta)} \left(dQ + \frac{1}{E} \delta \sum \frac{mv^2}{2} \right) + S_2 - S_1,$$

and remarked that it would vanish in case of “reversible” transformations. The term $\delta \sum \frac{mv^2}{2}$ was nothing else but the infinitesimal change of the “living force” of the system as a whole. The principle of “equivalence between heat and work” could be written as

$$d\tau_e = E dQ + \delta \sum \frac{mv^2}{2} + E \delta U,$$

and the “uncompensated work” as

$$P = \frac{1}{E} \int_{(1)}^{(2)} \frac{1}{F(\vartheta)} (d\tau_e - E \delta U) + S_2 - S_1.$$

When the transformation is isothermal, $F(\vartheta) = \text{const.}$, and the last equation becomes

$$E F(\vartheta) P = E [U_1 - F(\vartheta) S_1] - E [U_2 - F(\vartheta) S_2] + \int_{(1)}^{(2)} d\tau_e,$$

The uncompensated work is the sum of two terms: the work done by external forces, and “the opposite of the variation of a *uniform* function qualifying the state of the

system”. The uniform function was nothing else but a generalisation of the potential Duhem had introduced in 1886, namely

$$\mathcal{F} = E[U - F(\vartheta)S].$$

He reminded the reader that this generalised “*potentiel thermodynamique interne*” corresponded to Massieu’s “*fonction caractéristique*”, Gibbs’ “*fonction de force à température constante*”, and Maxwell and Helmholtz’s “*énergie libre*”.¹²

A specific law of equilibrium followed:

“Dans toute transformation réalisable, le travail non compensé est positif. Par conséquent, *si un système, dont la température est maintenue constante, se trouve dans un état tel que toute modification isothermique virtuelle entraîne un travail non compensé négatif, le système est assurément en équilibre.*”

According to a proven procedure, Duhem went on with a further refinement: when even external forces depends on a potential Ω , the uncompensated work becomes

$$E F(\vartheta)P = E[U_1 - F(\vartheta)S_1] + \Omega_1 - E[U_2 - F(\vartheta)S_2] - \Omega_2,$$

and a new potential Φ can be introduced:

$$\Phi = E[U - F(\vartheta)S] + \Omega \quad \text{and} \quad E F(\vartheta)P = \Phi_1 - \Phi_2.$$

Both the uncompensated work and equilibrium could be expressed in terms of the new potential Φ :

¹² Duhem 1891, pp. 245-7. See also Duhem 1886, pp. 9-10.

“Le travail non compensé accompli dans une modification isothermique quelconque est alors la variation changée de signe d’une fonction uniforme de l’état du système ; nous donnerons à cette fonction le nom de potentiel thermodynamique du système.

D’après cette définition, si un système, dont la température est maintenue constante, se trouve dans un état tel que son potentiel thermodynamique ait une valeur minimum parmi toutes celles qu’il peut prendre à la même température, le système est en équilibre.”

As Duhem remarked, the functions U , S and Ω , being state functions, are well-defined except for an arbitrary constant; therefore the two potential $\mathcal{F}$ and Φ are defined apart from an expression of the kind $A\mathcal{F}(\vartheta)+B$, wherein A and B are arbitrary constants.¹³

In the next section, “Etude d’un système dont le potentiel thermodynamique est supposé connu”, Duhem confined himself to “infinitesimal, *reversible*, isothermal transformations”: as a consequence,

$$E\mathcal{F}(\vartheta)dP=0, \text{ or } -\delta\mathcal{F}+d\tau_e=0.$$

The last equation could be further developed:

$$A\cdot\delta\alpha+B\cdot\delta\beta+\dots+L\cdot\delta\lambda-\left(\frac{\partial\mathcal{F}}{\partial\alpha}\cdot\delta\alpha+\frac{\partial\mathcal{F}}{\partial\beta}\cdot\delta\beta+\dots+\frac{\partial\mathcal{F}}{\partial\lambda}\cdot\delta\lambda\right)=0,$$

$$\left(A-\frac{\partial\mathcal{F}}{\partial\alpha}\right)\cdot\delta\alpha+\left(B-\frac{\partial\mathcal{F}}{\partial\beta}\right)\cdot\delta\beta+\dots+\left(L-\frac{\partial\mathcal{F}}{\partial\lambda}\right)\cdot\delta\lambda=0.$$

The procedure led to a set of equations already displayed by Duhem in the first section:

¹³ Duhem 1891, pp. 247-8. In 1888 the potential of external forces was W : see Duhem 1888, pp. 3-4.

$$(25) \left\{ \begin{array}{l} A = \frac{\partial}{\partial \alpha} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \\ B = \frac{\partial}{\partial \beta} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \\ \dots \dots \\ L = \frac{\partial}{\partial \lambda} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta) \end{array} \right. , \quad (26) \quad \Theta = f_{\vartheta}(\alpha, \beta, \dots, \lambda, \vartheta), \text{ and}$$

$$(27) \left\{ \begin{array}{l} R_{\alpha} = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \alpha} - \frac{\partial A}{\partial \vartheta} \right) \\ R_{\beta} = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \beta} - \frac{\partial B}{\partial \vartheta} \right) \\ \dots \dots \\ R_{\lambda} = \frac{1}{E} \frac{F(\vartheta)}{F'(\vartheta)} \left(\frac{\partial \Theta}{\partial \lambda} - \frac{\partial L}{\partial \vartheta} \right) \end{array} \right. .^{14}$$

According to Duhem, “the mechanical determination of the system” required firstly the specification of the function $\mathcal{F}$, and then the deduction of the generalized forces A , B , ..., 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 had *mechanical* and *thermal* components. 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 $n+1$ functions A , B , ..., L , and Θ , and the $n+1$ functions R_{α} , R_{β} , ..., R_{λ} , and R_{ϑ} depended on the whole set of parameters α , β , ..., λ and ϑ .

The formal resemblance between thermodynamics and mechanics was even deeper than Duhem explicitly stated. The Lagrangian generalization of space-time mechanical representation required n generalized parameters α , β , ..., and λ , and a time component t . In mechanical tradition, the parameter t played a double role: as an independent parameter, placed alongside the spatial parameters, and as basic parameter, which all the spatial parameters depended on. At that stage, Duhem did not explicitly take into account time: it played merely the role of basic implicit parameter. The role of

¹⁴ Duhem 1891, pp. 249-50.

independent parameter, on equal terms with regard *mechanical* parameters, was played by the *thermal* parameter ϑ .

Duhem was then ready to attain a satisfactory generalization of the design outlined in 1886: the derivation of mechanical and thermal feature of the system from the potential $\mathcal{F}$ and the function $\Theta = f_{\vartheta}(\alpha, \beta, \dots, \lambda, \vartheta)$. Apart from generalized forces and generalized thermal coefficients, three physical quantities waited for being derived: U , S and $R_{\vartheta} = C$.

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 too easy the derivation: 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:

“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.

Les égalités (27), (28), (29), (30) ont été démontrées en supposant que les égalités (25) et (26) étaient vérifiées, c'est-à-dire que le système était soumis aux forces extérieures qui en assurent l'équilibre.

Cette restriction devra toujours être observée lorsqu'on voudra faire usage des égalités (27) and (30). Mais nous allons voir que les égalités (28) et (29) peuvent, au contraire, être démontrées sans faire aucune hypothèse sur les forces extérieures auxquelles le système est soumise”¹⁵

Once again, at the end of the section, Duhem took into account the simplified case of purely thermal transformations, wherein the variation of ϑ did not affect the other parameters, and $\Theta = f_{\vartheta} = 0$. That choice, combined with the choice $\vartheta = T$ and $F(\vartheta) = T$,

¹⁵ Duhem 1891, pp. 250-1. 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). The analysis of Duhem's derivations and the correct derivations can be found in the *Appendix*.

led to the a set of very simple equation for the functions R_α , R_β , ..., R_λ , and C , already deployed at the end of the first section. There was, nevertheless, an important difference: consistently with the content of the present section, those functions were expressed in terms of the potential $\mathcal{F}$:

$$\left\{ \begin{array}{l} R_\alpha = -\frac{T}{E} \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial T} \\ R_\beta = -\frac{T}{E} \frac{\partial^2 \mathcal{F}}{\partial \beta \partial T} \\ \dots\dots\dots \\ R_\lambda = -\frac{T}{E} \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial T} \\ C = -\frac{T}{E} \frac{\partial^2 \mathcal{F}}{\partial T^2} \end{array} \right. .$$

Moreover, as expected,

$$U = \frac{1}{E} \left(\mathcal{F} - T \frac{\partial \mathcal{F}}{\partial T} \right)_{16}$$

$$S = -\frac{1}{E} \frac{\partial \mathcal{F}}{\partial T}$$

In the last section of his 1891 paper, “D’un changement de variable”, Duhem outlined an even more abstract 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: there was a sort of symmetry between initial and final steps. 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 , Duhem showed that we can start from the *dynamical-thermal* parameters A ,

¹⁶ Duhem 1891, p. 257.

$B, \dots, L$, and ϑ , in order to arrive at the *geometrical* equations of equilibrium on $\alpha, \beta, \dots$, and λ .¹⁷

The methods of Analytic Mechanics, or rational mechanics, were fully exploited by Duhem in the perspective of a rational thermodynamics. Had something like *crisis of mechanics* ever troubled physicists at the end of the nineteenth century, that alleged crisis would not have dwelled at Duhem's home. Since the 1880s, Duhem had pursued a new alliance between Lagrangian mechanics and the science of heat, and that pursuit was not an isolated task. In the same years, in British islands, G.F. FitzGerald, J.J. Thomson and J. Larmor were looking for a new alliance between Lagrangian mechanics and the science of electromagnetic phenomena. On the Continent, H.A. Lorentz was undertaking a similar task, which would have led him to a sort of a geometrization of time in 1895. A new alliance between Analytic Mechanics and a field theory purified by the concept of force led Hertz to a wider-scope, although very formal, design of geometrization of physics in 1894.¹⁸

The fact is that, in the history of mechanics, we see two different traditions: the tradition of mechanical models and machinery, on the one hand, and Lagrange and Hamilton's abstract mechanics, on the other. In its turn, the former could be split into different sub-traditions: the kinetic model of matter and motion, the theoretical model of forces between microscopic particles, and the theoretical model of fields of force having their set in space. As Hertz remarked in 1892, even intermediate models were at stake in the context of electromagnetic theories.¹⁹ Duhem can be definitely enrolled in the latter

¹⁷ Duhem 1891, pp. 259-61.

¹⁸ Hertz 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". He was not principally interested in mathematical details: what he considered new and more interesting in his reconstruction of mechanics was "the logical and philosophical aspect of the matter". On the one hand, he set up a theory by means of definitions, theorems and differential equations. On the other hand, he acknowledged that a theory required a conceptual representation, or a rational *invention*, in order to be put in correspondence with nature. A theory is a good representation, he stated, when the relationships among the abstract symbols of the representation correspond to the relationships among the real entities associated to those symbols. 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.

¹⁹ Hertz deployed four theoretical models: the first consisted of traditional action at a distance, and the second corresponded to the so-called "potential theory", where "an acting body is still both the seat and the source of the force". The third took into account the polarisation of the medium and "is represented by Helmholtz's theory". Nevertheless, that model could be further split into two sub-models (say 3a and 3b), according to the relative weight given to "an influence due to direct action-at-a-distance, and an influence due to the intervening medium". In the limiting case (3b), when polarisation overwhelmed action at a distance, "the whole of the

tradition, whereas the British Rankine, Maxwell, J.J. Thomson and Larmor, as well as other Continental physicists, skipped from the former to the latter. If something like a *crisis of Mechanics* can be found in the late nineteenth century, it was only a crisis of the former tradition. As mentioned in the “Foreword”, the meta-theoretical debate between the upholders of the two traditions was one of the consequences of the emergence of theoretical physics, which triggered off the widening of the scientific horizon. That meta-theoretical debate seems to me something more complex than a mere *crisis*, even though the choice of the label *crisis* could be looked upon as a convenient simplification.

Duhem’s design had a double 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 or meta-theoretical commitments: neither Boltzmann nor Duhem’s general attitudes towards Mechanics can be associated to whatsoever *crisis of mechanics*.

energy” was in the medium. According to Hertz, this case resembled Maxwell’s theory, but, he claimed, the resemblance was misleading. Maxwell’s theory corresponded to a fourth model, where actions at a distance had to be definitely denied. See Hertz H. 1892, in Hertz H. 1962, pp. 22-6. For a discussion of theoretical and meta-theoretical issues in Hertz classification, see Bordoni S. 2008, pp. 80-3.

10. The generalised Mechanics of a “complex system”

In 1892 Duhem submitted to the *Journal de mathématiques pures et appliquées* a long paper with the very general title “Commentaires aux principes de la Thermodynamique”. It was the first part of a sort of trilogy whose second and third part were hosted by the *mathematical* journal in 1893 and 1894 respectively. The set of the three papers, when considered as a whole, was nothing less than a treatise on thermodynamics. The first passages of the first paper let a wide historical and philosophical perspective emerge: 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 incapable d’aborder. A ce moment, il devient nécessaire de revenir aux fondements sur lesquels repose la science, d’examiner à nouveaux 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 the researches on Thermodynamics: at that time, the end of the nineteenth century,

¹ Duhem 1892a, p. 269. Duhem’s representation of the history of science as a periodical series of ordinary applications and deep transformations has been subsequently exploited by historians of science. After seventy years, in the course of a very different season of history of science, Kuhn’s representation of a periodical series of “normal” science and “revolutionary” science followed objectively Duhem’s track. See, for instance, Kuhn T.S. 1962, in Kuhn T.S. 1996, pp. 10 and 111.

a deep “reconsideration of the principles was needed”. He was trying to submit such a review “to the readers of the *Journal de mathématiques*”. Before developing his theoretical design, Duhem expressed some meta-theoretical cogitation, even though they could be looked upon 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”. Duhem acknowledged that different theoretical approaches to Thermodynamics could be “equally satisfactory, even more satisfactory” than his own. There was a plurality of theories able to describe a given set of phenomena in a consistent way.²

In the first chapter, “Définitions préliminaires”, dealing with the geometrical and kinematical foundations of physics, we find the equivalence between different theoretical representations of a given set of phenomena once again. In particular, Duhem found arbitrary every hypothesis on the ultimate representation of matter, and basically equivalent the opposite theoretical models of continuity and discontinuity, even though he preferred the former.

“*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. Pur 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 première 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

² Duhem 1892a, p. 270. It seems to me 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.”

³ Duhem 1892a, p. 272.

Duhem remarked that, sometimes, some theoretical representation was 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.⁴

He stressed 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, kinematical parameters to the second one. He qualified the former as those which “define the nature of the system”, and the latter as those which “define the state”. He labelled $A, B, \dots$, and L the elements of the first set, and $\alpha, \beta, \dots$, and λ the elements of the second set. He called “*virtual transformation*” the “purely intellectual procedure” representing the continuous series of steps leading from a given initial state to a given final state.

A given fragment of matter could be geometrically identified by functions of $\alpha, \beta, \dots, \lambda$, and its velocity by their corresponding time derivatives:

$$(1) \begin{cases} x = \varphi(\alpha, \beta, \dots, \lambda) \\ y = \psi(\alpha, \beta, \dots, \lambda) \\ z = \chi(\alpha, \beta, \dots, \lambda) \end{cases} \quad \text{and} \quad (2) \begin{cases} \frac{dx}{dt} = \frac{d\varphi}{d\alpha} \frac{d\alpha}{dt} + \frac{d\varphi}{d\beta} \frac{d\beta}{dt} + \dots + \frac{d\varphi}{d\lambda} \frac{d\lambda}{dt} \\ \frac{dy}{dt} = \frac{d\psi}{d\alpha} \frac{d\alpha}{dt} + \frac{d\psi}{d\beta} \frac{d\beta}{dt} + \dots + \frac{d\psi}{d\lambda} \frac{d\lambda}{dt} \\ \frac{dz}{dt} = \frac{d\chi}{d\alpha} \frac{d\alpha}{dt} + \frac{d\chi}{d\beta} \frac{d\beta}{dt} + \dots + \frac{d\chi}{d\lambda} \frac{d\lambda}{dt} \end{cases}$$

Among the state quantities Duhem distinguished those which explicitly appear in the above equations from those which do not appear. He reserved the labels $\alpha, \beta, \dots$, and λ for the former, and introduced new labels $a, b, \dots, l$ for the latter: in some way he separated geometrical quantities from other quantities.⁵

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 was not an additive quantity.

⁴ Duhem 1892a, p. 274.

⁵ Duhem 1892a, pp. 276 and 278-9,

Temperature could not literally *measure*, but only *locate* the different levels of heat. Moreover, temperature could not be univocally defined: if we called it ϑ , every continuous and increasing function $\Theta = f(\vartheta)$ could play the role of temperature. However defined, temperature could replace the concept of “equally warm” in the definition of equilibrium: “if an isolated system is in equilibrium, the temperature ϑ has the same value everywhere”.⁶

In the second chapter, Duhem 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 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.⁷

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 $\mathcal{T}$ and $\mathcal{T}'$ of S and S' , the potential energy could not consist only of the sum of the two isolate potential energies U and U' of S and S' , but had to contain a term of *interaction*.

$$\begin{aligned}
 Y &= U(\alpha, \beta, \dots, \lambda; a, b, \dots, l) \\
 (1) \quad &+ U'(\alpha', \beta', \dots, \lambda'; a', b', \dots, l') \\
 &+ \Psi(\alpha, \beta, \dots, \lambda; a, b, \dots, l; \alpha', \beta', \dots, \lambda'; a', b', \dots, l')
 \end{aligned}$$

The total energy of Σ was therefore

$$(2) \quad \varepsilon = Y + \frac{1}{E}(\mathcal{T} + \mathcal{T}').$$

Then Duhem defined two sets of quantities derived from the potential of interaction Ψ :

⁶ Duhem 1892a, pp. 284 and 286-8. According to Duhem, temperature stemmed from the concept of “equally warm”, and the equilibrium of an isolated system required that “every material component of the system be equally warm”.

⁷ Duhem 1892a, pp. 291-307.

$$(4) \quad \begin{cases} E \frac{\partial \Psi}{\partial \alpha} = -A, \\ E \frac{\partial \Psi}{\partial \beta} = -B, \\ \dots \dots \\ E \frac{\partial \Psi}{\partial \lambda} = -L, \end{cases} \quad \begin{cases} E \frac{\partial \Psi}{\partial a} = -\mathcal{A}, \\ E \frac{\partial \Psi}{\partial b} = -\mathcal{B}, \\ \dots \dots \\ E \frac{\partial \Psi}{\partial l} = -\mathcal{L}, \end{cases}$$

The first set corresponded to “the *forces*”, and the second set to “the *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 separations of Lagrangian parameters into geometrical parameters and state parameters. After having defined the generalized velocities

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

Duhem could therefore represent the works done by forces and influences as

$$(A \cdot u + B \cdot v + \dots + L \cdot w) dt \quad \text{and} \quad (\mathcal{A} \cdot \varphi + \mathcal{B} \cdot \chi + \dots + \mathcal{L} \cdot \psi) dt.^8$$

The potential of interaction Ψ deserved some additional mathematical and physical remarks:

“Ainsi le travail des actions du système S’ sur le système S n’est pas, en générale, 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’.*

⁸ Duhem 1892a, pp. 308-9 and 311. Unfortunately, the “forces” and the parameters representing the “nature” of the system were labelled by the same letters.

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.”⁹

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 $S_1, S_2, \dots, S_n$ ”. Conversely, those definitions and remarks allowed Duhem to begin to draft, at least in part, the features of a “complex system”.

“Dans un système complexe, formé de plusieurs systèmes indépendants, chacun de ces dernières subit certaines actions de la part de l'ensemble des autres ; toutes ces actions, prise 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.”*¹⁰

The key entity was the total energy

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

and the key procedure was the correct computation of the variations δY and $\delta(\mathcal{T} + \mathcal{T}')$. In accordance with a well-known procedure in analytic mechanics, the second variation took the form

$$\delta(\mathcal{T} + \mathcal{T}') = - \left[\left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) u + \dots + \left(\frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial w} \right) w + \left(\frac{\partial \mathcal{T}'}{\partial \alpha'} - \frac{d}{dt} \frac{\partial \mathcal{T}'}{\partial u'} \right) u' + \dots + \left(\frac{\partial \mathcal{T}'}{\partial \lambda'} - \frac{d}{dt} \frac{\partial \mathcal{T}'}{\partial w'} \right) w' \right] dt.$$

⁹ Duhem 1892a, pp. 312-3.

¹⁰ Duhem 1892, p. 315.

Obviously, the kinetic terms depended only on the geometrical parameters $\alpha, \beta, \dots$, and λ , while the potential terms also depended on the *state* parameters $a, b, \dots$, and l . As a consequence, to the variation δY corresponded quite a complicated expression:

$$\delta Y = \left[\begin{aligned} &\left(\frac{\partial U}{\partial \alpha} + \frac{\partial \Psi}{\partial \alpha} \right) u + \dots + \left(\frac{\partial U}{\partial \lambda} + \frac{\partial \Psi}{\partial \lambda} \right) w + \left(\frac{\partial U}{\partial a} + \frac{\partial \Psi}{\partial a} \right) \varphi + \dots + \left(\frac{\partial U}{\partial l} + \frac{\partial \Psi}{\partial l} \right) \psi \\ &+ \left(\frac{\partial U'}{\partial \alpha'} + \frac{\partial \Psi}{\partial \alpha'} \right) u' + \dots + \left(\frac{\partial U'}{\partial \lambda'} + \frac{\partial \Psi}{\partial \lambda'} \right) w' + \left(\frac{\partial U'}{\partial a'} + \frac{\partial \Psi}{\partial a'} \right) \varphi' + \dots + \left(\frac{\partial U'}{\partial l'} + \frac{\partial \Psi}{\partial l'} \right) \psi' \end{aligned} \right] dt$$

The expanded form of $\delta \varepsilon = 0$ therefore became

$$(3) \quad \delta \varepsilon = \left[\left(\frac{\partial U}{\partial \alpha} + \frac{\partial \Psi}{\partial \alpha} \right) - \frac{1}{E} \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) \right] u + \dots + \left(\frac{\partial U}{\partial a} + \frac{\partial \Psi}{\partial a} \right) \varphi + \dots + \left[\left(\frac{\partial U'}{\partial \alpha'} + \frac{\partial \Psi}{\partial \alpha'} \right) - \frac{1}{E} \left(\frac{\partial \mathcal{T}'}{\partial \alpha'} - \frac{d}{dt} \frac{\partial \mathcal{T}'}{\partial u'} \right) \right] u' + \dots + \left(\frac{\partial U'}{\partial a'} + \frac{\partial \Psi}{\partial a'} \right) \varphi' + \dots = 0 \quad .^{11}$$

Three kinds of contribution to energy were at stake: a kinetic or *inertial* contribution, involving the derivatives of the living forces $\mathcal{T}$ and $\mathcal{T}'$, internal energies, involving the derivatives of U and U' , and energy of interaction, involving the derivatives of the interaction potential Ψ . The second and third contribution split into two components: an ordinary mechanical component and a component corresponding to the physical state of the system. The partial systems S and S' contributed to energy in a symmetric way: $\delta \varepsilon = dQ + dQ'$, and therefore $dQ + dQ' = 0$. Duhem was following the track of his 1891 paper, wherein heat was the sum of both mechanical and thermal work. In 1892 he generalized the concept, and heat became the sum of the effects due to *inertial* actions, forces, and *influences* of every kind. Both ordinary motions and changes of state contributed to heat, according to a more general rational mechanics.

Heat had a relational nature: in a “complex isolated system, consisting of two independent systems S and S' , ... one of them send out as much heat as the other

¹¹ Duhem 1892a, p. 310.

receive”. The concept of an isolated body placed in an empty space, and sending out or receiving heat, seemed to Duhem “not consistent with the definition given above”. According to Duhem, heat means exchange of heat: heat requires some sort of interaction between different bodies, or at least between a body and the surrounding aether.¹²

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

$$(12) \quad E R_\alpha = \left(E \frac{\partial U}{\partial \alpha} - A \right) - \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right),$$

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

$$(13) \quad dQ = - \left[(R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots R_\lambda \cdot \delta\lambda) + (\mathcal{R}_a \cdot \delta a + \mathcal{R}_b \cdot \delta b + \dots + \mathcal{R}_l \cdot \delta l) \right].$$

In the right side of the last equation, the first bracket contains the effect of mechanical actions, and the second the effects of other kinds of *influences*: they were a generalization of the term R_θ 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 its turn, the virtual work depended on both the “actions exerted on the system S” and “inertial forces” on S. In reality, virtual work was the sum of three components, since actions split into *forces* and *influences*. We have therefore $d\tau = d\tau_1 + d\tau_2 + d\tau_3$, wherein

$$(14) \quad d\tau_1 = (A \cdot \delta\alpha + \dots), \quad d\tau_2 = (\mathcal{A} \cdot \delta a + \dots),$$

$$(15) \quad d\tau_3 = \left[\left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) \delta\alpha + \dots \right].$$

¹² Duhem 1892a, pp. 319-20.

The comparison between equations(12/13) and (14/15) led to the fundamental equation,

$$(16) \quad E(dQ + \delta U) = d\tau,$$

which was nothing else but the first principle of Thermodynamics or “the law of equivalence between heat and work”.¹³

Once again, in the last part of the chapter, Duhem stressed the relational conception of heat.

“Lorsqu’un système est formé de plusieurs parties indépendantes, la quantité de chaleur qu’il dégage dans une modification virtuelle quelconque est égale à la somme algébrique des quantités de chaleur que ses diverses parties dégagent dans la même modification.

Ce théorème nous sera utile dans la suite.

Ici vient naturellement se placer une réflexion semblable à celle que nous a suggéré 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 sense.”¹⁴

According to Duhem’s design, his generalised Mechanics was, at the same time, an Analytic Thermodynamics, and ordinary mechanics should have been nothing else but one of its specific applications. In order to derive ordinary mechanics from that wide-scope Mechanics/Thermodynamics, he assumed that $dQ=0$, and all “thermal coefficients” vanish.

¹³ Duhem 1892a, pp. 320-1.

¹⁴ Duhem 1892a, p. 323.

In this case, equations (12) become

$$(18) \quad \left(E \frac{\partial U}{\partial \alpha} - A \right) - \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) = 0 ,$$

$$(18bis) \quad E \frac{\partial U}{\partial a} - \mathcal{A} = 0 .$$

Since the first equation corresponds to Lagrange's equation of rational mechanics, the derivation seems 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, then all thermal coefficients vanish? At that stage, Duhem could not satisfactorily answer the question, and further theoretical investigations were required.

“On reconnaît les équations du mouvement d'un système dans lequel les frottements sont nuls ; dans le cas que l'on étudie ordinairement en Mécanique, il n'existe pas d'autres variables que celles qui figurent dans les équations (1) du chapitre I ; il n'existe donc pas d'équations du type (18bis) ; toutes les équations qui régissent le mouvement du système ont la forme (18), donnée, on le sait, par Lagrange.

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.”¹⁵

¹⁵ Duhem 1892a, p. 324.

Indeed, it is questionable whether the vanishing of the “thermal coefficients” and the condition $dQ=0$ are equivalent statements. At the end of Duhem 1892 paper, the nature of the relationship between Mechanics and Thermodynamics was waiting for a complete clarification.

The following year Duhem published the second part of his *Commentaire*. As in the 1892 first part, the first chapter was devoted to some preliminary definitions and remarks. He faced the apparently inconsistent concept of “transformations which consist of a series of states of equilibrium”. He tried to give it “a logic meaning”, by making resort to the difference between geometrical parameters and state parameters. A physical system can 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.¹⁶

The last issue concerned “the concept of reversible transformation”, one of “the most important and, at the same time, most problematic to be defined in Thermodynamics”, as Duhem remarked. 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.”¹⁷

In reality, the whole 1893 *Commentaire* consists of a net of preliminary specifications and detailed remarks on heat, entropy, and the second Principle of Thermodynamics. There are “*infinite reversible transformations*” leading a physical system from a state $(\alpha, \beta, \dots, \lambda, \text{ and } \vartheta)$ to a new state $(\alpha', \beta', \dots, \lambda', \text{ and } \vartheta')$. For every reversible transformation, the integral

¹⁶ See Duhem 1893a, pp. 302-4, in particular p. 304: “Pour qu’une modification réelle soit une succession d’états d’équilibre, il est nécessaire, mais non suffisant, que tous les points du système gardent une position invariable dans l’espace pendant toute la durée de cette modification.

Or est-il absurde d’admettre l’existence d’une modification durant laquelle tous les points du système gardent une position invariable ? Evidemment non ; on est parfois amené, en Physique, à imaginer de semblables modifications. Prenons, par exemple, un récipient renfermant un mélange d’hydrogène et de chlore ; la combinaison se produit ; une modification, un changement d’état a lieu ; cependant, on peut fort bien admettre que la matière qui remplissait chacun des éléments de volume du récipient au début de la combinaison est demeurée dans le même élément de volume pendant toute la durée de la modification”.

¹⁷ Duhem 1893a, pp. 305-7, in particular p. 307.

$$\int \frac{dQ}{F(\vartheta)}$$

has the same value: in case of reversible cycles, the integral vanishes. It is nothing else but the entropy of the system.

The specific case of ordinary mechanics was looked upon by Duhem as particularly important, for it was a specific application of his generalized Mechanics/Thermodynamics. Once again, when $R_\alpha = R_\beta = \dots = R_\lambda = 0$, automatically $dQ = 0$, and

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

This was the case of “classical rational Mechanics”, wherein no reference to heat or temperature is taken.¹⁸ The fact is that, in this case, the concept of entropy and the second Principle lost their meaning: if the mathematical derivation of Mechanics from Thermodynamics could be successfully performed, the conceptual relationship between Mechanics and Thermodynamics was an open question.

It is worth mentioning that, in the same year, Poincaré published some notes just 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”: amount and direction of their velocity could not change unless “two atoms collide”. In the second case, atoms are imaged as submitted a mutual “attraction (or repulsion), depending on their distance, and according to some law”. For he saw the first conception as a “particular case of the second”, he would have disregarded the distinction in the course of the paper. Moreover, he would have

¹⁸ Duhem 1893a, pp. 337, 345, 355, and 357-8.

confined himself to the comparison between the “hindrances faced by the mechanists” and “experimental data”.¹⁹

According to Poincaré, Mechanics required that “all phenomena are *reversible*” with regard to time: in a sharper way, “reversibility is a necessary consequence of every mechanical hypothesis”. The fact is that any experiences contrasted that requirement: thermal conduction was a well-known instance of irreversibility. That “a cold body gives back the heat it 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 cannot pass from B to A, “neither through the same path, nor through a different path”. The attempts to escape this contradiction appeared “not sufficient” to Poincaré, Helmholtz hypothesis of “hidden motions” included.²⁰

The recent developments of Mechanics, due to Poincaré himself, had showed 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 should drift towards “a given final state, where it will never come back from”. 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 will 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 had expected thermal irreversibility stem from the laws of Mechanics, seemed to Poincaré a basic inconsistency: no logical procedure let us assemble a deduction wherein “we find reversibility at the outset, and irreversibility at the end”.²¹

In 1894, in the third part of the *Commentaire*, Duhem returned to 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 α , β , ..., λ and ϑ , which seemed a step backward with regard to the more general choice of

¹⁹ Poincaré H. 1893, p. 534.

²⁰ Poincaré H. 1893, pp. 534-5.

²¹ Poincaré H. 1893, pp. 536-7.

parameters $\alpha, \beta, \dots, \lambda, a, b, \dots, l$ he had introduced in 1892.²² Nevertheless, soon afterwards, he tried another kind of generalization: he took into account a “complex system” consisting of two “different and independent components”, whose internal energy, entropy, and thermodynamic potential were respectively

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

As in Duhem’s 1892 approach, the internal energy U of the complex system involved an interaction term $X_{1/2}$:

$$U = Y_1(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1) + Y_2(\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2) + X_{1/2}(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1; \alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2).$$

Then he undertook a step forward: he took into account “foreign bodies” or “external bodies”, in some way some kind of *environment*. The global internal $\mathcal{U}$ energy had another kind of interaction term Ψ :

$$\mathcal{U} = U + U' + \Psi,$$

wherein U' was the internal energy of the environment.²³

When we take into account the forces acting on each components of the complex system, we find both the potentials $X_{1/2}$ and Ψ :

$$(11) \quad \begin{aligned} A_1 &= -E \frac{\partial}{\partial \alpha_1} (X_{1/2} + \Psi), \dots, \Theta_1 = -E \frac{\partial}{\partial \vartheta_1} (X_{1/2} + \Psi) \\ A_2 &= -E \frac{\partial}{\partial \alpha_2} (X_{1/2} + \Psi), \dots, \Theta_2 = -E \frac{\partial}{\partial \vartheta_2} (X_{1/2} + \Psi) \end{aligned}$$

²² Duhem 1894, pp. 208-10.

²³ Duhem 1894a, pp. 210-11. The new term $X_{1/2}$ corresponded to the old term Ψ Duhem had used 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 equilibrium of the complex system required, on the one side, that

$$(12) \quad \vartheta_1 = \vartheta_2 = \vartheta ,$$

wherein ϑ was the temperature of the rest of the environment: this assured thermal equilibrium, or the thermal side of equilibrium. On the other side, there were the mechanical/thermodynamic conditions of equilibrium expressed in terms of the thermodynamic potentials. In other words,

$$(13) \quad \begin{aligned} \frac{\partial \mathcal{F}_1}{\partial \alpha_1} = -E \frac{\partial}{\partial \alpha_1} (X_{1/2} + \Psi), \dots, \frac{\partial \mathcal{F}_1}{\partial \vartheta_1} = -E \frac{\partial}{\partial \vartheta_1} (X_{1/2} + \Psi) - E F'(\vartheta_1) \Sigma_1 \\ \frac{\partial \mathcal{F}_2}{\partial \alpha_2} = -E \frac{\partial}{\partial \alpha_2} (X_{1/2} + \Psi), \dots, \frac{\partial \mathcal{F}_2}{\partial \vartheta_2} = -E \frac{\partial}{\partial \vartheta_2} (X_{1/2} + \Psi) - E F'(\vartheta_2) \Sigma_2 \end{aligned}$$

When the equilibrium is satisfied, Duhem noticed, a single “internal thermodynamic potential” $\mathfrak{F}$ and a single entropy S can be associated to the complex system. Since $\mathcal{F}_1$ does not depend on $(\alpha_2, \beta_2, \dots, \lambda_2, \vartheta_2)$, as well as $\mathcal{F}_2$ does not depend on $(\alpha_1, \beta_1, \dots, \lambda_1, \vartheta_1)$, equations (13) become

$$\begin{aligned} E \frac{\partial \Psi}{\partial \alpha_1} = -\frac{\partial}{\partial \alpha_1} (E X_{1/2} + \mathcal{F}_1 + \mathcal{F}_2), \dots, E \frac{\partial \Psi}{\partial \vartheta_1} = -\frac{\partial}{\partial \vartheta_1} (E X_{1/2} + \mathcal{F}_1 + \mathcal{F}_2) - E F'(\vartheta_1) \Sigma_1 \\ E \frac{\partial \Psi}{\partial \alpha_2} = -\frac{\partial}{\partial \alpha_2} (E X_{1/2} + \mathcal{F}_1 + \mathcal{F}_2), \dots, E \frac{\partial \Psi}{\partial \vartheta_2} = -\frac{\partial}{\partial \vartheta_2} (E X_{1/2} + \mathcal{F}_1 + \mathcal{F}_2) - E F'(\vartheta_2) \Sigma_2 \end{aligned} \quad .^{24}$$

If we define $\mathfrak{F} = \mathcal{F}_1 + \mathcal{F}_2 + E X_{1/2}$, then we have

$$E \frac{\partial \Psi}{\partial \alpha_1} = -\frac{\partial \mathfrak{F}}{\partial \alpha_1}, \dots; \quad E \frac{\partial \Psi}{\partial \alpha_2} = -\frac{\partial \mathfrak{F}}{\partial \alpha_2} \dots$$

²⁴ Duhem 1894a, pp. 212-5.

“Lorsqu’un système est formé de plusieurs parties indépendantes, toutes à la même température, le potentiel thermodynamique interne du système s’obtient en faisant la somme des potentiels thermodynamiques internes des parties, et en y ajoutant l’une des déterminations du potentiel des actions mutuelles de ces parties, celle qui s’annule lorsqu’on éloigne infiniment ces parties les unes des autres.”²⁵

In the second chapter, Duhem returned to the more general choice of parameters $\alpha, \beta, \dots, \lambda, a, b, \dots, l$ he had introduced in 1892, in the first part of the *Commentaire*. The first passage of the chapter strikes the reader because of the reference to an Aristotelian conception 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 passage:

“Nous prenons, dans ce Chapitre, le mot *mouvement* pour désigner non seulement un changement de position dans l’espace, mais encore un changement d’état quelconque, lors même qu’il ne serait accompagné d’aucun déplacement. Ainsi, il y aurait mouvement si les variables que nous avons désignées par $a, b, \dots, l$... variaient seules, les variables $\alpha, \beta, \dots, \lambda$ gardant des valeurs fixes. De la sorte, le mot *mouvement* s’oppose non pas au mot *repos*, mais au mot *équilibre*.”²⁶

Duhem reminded the reader about the equation for the equilibrium for a mechanical-thermodynamic system he had introduced in the third chapter of 1892 first Part, apart from the usual symbolic difference:

$$(1) \quad A' - \frac{\partial \mathcal{F}}{\partial \alpha} + \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} \right) = 0, \dots, L' - \frac{\partial \mathcal{F}}{\partial \lambda} + \left(\frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} \right) = 0. \quad ^{27}$$

²⁵ Duhem 1894a, p. 217.

²⁶ Duhem 1894a, p. 222.

²⁷ Duhem 1894a, p. 223. When comparing these equations with those appearing in Duhem’s 1892 paper, the external forces $A, B, \dots, L$ are now replaced by $A', B', \dots, L'$, and the coordinates derivatives $u, v, \dots, w$ by $\alpha', \beta', \dots, \lambda'$. The slight difference between the forces A and A' can be found in the explicit dependence on time in the latter.

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. He introduced new functions $f_\alpha, f_\beta, \dots, f_\lambda$, which generalized the last equations in the following way:

$$(2) \quad A' - \frac{\partial \mathcal{F}}{\partial \alpha} + \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} \right) = -f_\alpha, \dots, L' - \frac{\partial \mathcal{F}}{\partial \lambda} + \left(\frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} \right) = -f_\lambda.$$

The reader could be stunned by the labels attached to the terms expressing non-equilibrium: “passive resistances to be overcome by the system”. Those resistance depended on the basic parameters $\alpha, \beta, \dots, \lambda, \vartheta$, their time derivatives $\alpha', \beta', \dots, \lambda'$ and the time t : from the mathematical point of view, they were “resistances” in the usual mechanical sense. In this perspective, equilibrium was *disturbed* by some kind of generalized *friction*: a corresponding work $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$ could be associated to that kind of forces. Although the subject Duhem was facing dealt with a generalized thermodynamic, he choose the traditional tools of rational Mechanics and the traditional mechanical lexicon. This choice could be looked upon as a short-sighted approach, but the fact is that he had just transformed the meaning of mechanical concepts into a new, generalized, and Aristotelian-flavoured physics.²⁸

The formal reduction of a generalized thermodynamic problem to a generalized mechanical problem, even though in a rephrased Aristotelian perspective, could not give the solution of the problem. The fact is that the n last equations depend on the $n+1$ Lagrangian parameters $\alpha, \beta, \dots, \lambda$, and ϑ , and Duhem had not at his disposal a mechanical generalization for the equation corresponding to the parameter ϑ .

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

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

²⁸ Duhem 1894a, pp. 223-4. In this case the symbolic mismatch seems even more puzzling: in 1891 Duhem had made use of the functions $f_\alpha, f_\beta, \dots, f_\lambda$ in order to express explicitly the dependence of external forces on the basic parameters, namely $A = f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta)$ and so on. In 1894, the new *dissipative forces* $f_\alpha, f_\beta, \dots, f_\lambda$ had to be added to the already existing forces $A', B', \dots, L'$.

Les équations (2) deviennent lors des équations différentielles du seconde ordre, qui détermineraient les valeurs des variables α , β , ..., λ , ϑ , 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.”²⁹

Duhem was forced to look for the lacking equation outside the field of his generalized Mechanics/Thermodynamics. The fact is that purely thermal processes, involving only temperature change over time, were hard to include in his generalisation.

Nevertheless, he tried to attain a further generalization of the “thermal coefficients” he had introduced in 1891, and generalized in the third chapter (eq. 12) of the first Part of his *Commentaire*. 1891 and 1892 versions of thermal coefficients were respectively

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

and the updated version was only slightly different, in order to account for the new generalized resistances:

$$(3) \quad E R'_{\alpha} = \left(E \frac{\partial U}{\partial \alpha} - A' \right) - \left(\frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) + f_{\alpha}, \dots\dots\dots$$

The equivalent 1891 version

²⁹ Duhem 1894a, pp. 224-5.

$$\frac{R_\alpha}{F(\vartheta)} = -\frac{\partial S}{\partial \alpha}, \dots, \frac{R_\vartheta}{F(\vartheta)} = -\frac{\partial S}{\partial \vartheta}$$

became in 1894 nothing more than

$$(4) \quad E R'_\alpha = E F(\vartheta) \frac{\partial S}{\partial \alpha} + f_\alpha, \dots, E C' = E F(\vartheta) \frac{\partial S}{\partial \vartheta},$$

$$\text{namely } (5) \quad R'_\alpha = R_\alpha + \frac{f_\alpha}{E}, \dots, C' = C.$$

In the last series of equations, in the ϑ component, the term representing the passive resistance was missing. It was not put forward at the beginning, and it could not be found at the end. Duhem overestimated the result: the fact that the thermal capacity of a system, differently from the other thermal coefficients, was not affected by the difference between equilibrium and “motion” (in the generalized sense), was a mere consequence of his formal choice. In some way, *purely* thermal processes had been left out of the door from the outset.³⁰

According to the conceptual framework of a generalized Mechanics, he put forward a “fundamental hypotheses” on the passive *resistances* $f_\alpha, f_\beta, \dots, f_\lambda$: the work done by those resistances could be only null or negative. That hypothesis allowed Duhem to attain a meaningful result concerning the second Principle of Thermodynamics. In fact, from the last set of equations,

$$\begin{aligned} (9) \quad \frac{dQ}{F(\vartheta)} &= \frac{-[R'_\alpha \cdot \delta \alpha + \dots R'_\lambda \cdot \delta \lambda + C \cdot \delta \vartheta]}{E F(\vartheta)} \\ &= \frac{-[E F(\vartheta) dS + f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda]}{E F(\vartheta)} \\ &= -dS - \frac{f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda}{E F(\vartheta)}. \end{aligned}$$

³⁰ Duhem 1894a, pp. 225-6.

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

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

If

$$(8) \quad f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda \leq 0,$$

then

$$(10) \quad \int \frac{dQ}{F(\vartheta)} \geq 0.$$

Duhem identified the work $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$ with Clausius' "uncompensated work".

"Cette inégalité célèbre est due à Clausius.

Clausius a donnée à la quantité $-(f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda)$, qui est égale au travail des résistances passives changé de signe, et qui, par conséquent, n'est négative dans aucune modification réelle du système, le nom de travail non compensée accompli durant cette modification. La quantité $EF(\vartheta)dS$ est au contraire, pour lui, le travail compensé accompli durant cette même modification."³¹

A second meaningful result concerned entropy as well: in an isolated system, $dQ=0$, and equation (9) offered

³¹ Duhem 1894a, pp. 228-9.

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

Because of the positive value of the second side of the equation, the first side, namely entropy, was positive as well. No transformation involving an isolated system could therefore “make the entropy of the system increase”.³²

In the new theoretical framework, the generalization of the concept of passive resistances, or viscosity, or friction, paved the way leading from a generalized Mechanics to the core of Thermodynamics, namely the second Principle. The concept of thermal dissipation in natural phenomena was physically and mathematically dressed with the clothes of mechanical dissipation.

The second principle of Thermodynamics had therefore received a mechanical interpretation. But the 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 here a macroscopic mechanical re-interpretation, linked to a re-interpretation of the word “motion” in the context of a new Aristotelian perspective.

At the end of the third Part of his *Commentaire*, Duhem drafted some general “Conclusions”, wherein he put his approach to Mechanics and Thermodynamics into a historical perspective. He found two different trends in the relationship between Mechanics and 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”.

What had the former attained? They had managed to successfully interpret the first Principle, namely the Principle of conservation of energy, but had failed to explain the

³² Duhem 1894a, p. 229.

second Principle, “Carnot’s Principle”. In spite of the “daring efforts” of Clausius, Boltzmann and Helmholtz, “they had not managed to make Carnot’s principle stem from the laws of Dynamics in a satisfactory way”. According to Duhem, the latter had had more success: Kirchhoff had shown that Clausius’ preference for “Thermodynamics as an independent science” could be successfully pursued.³³

Duhem saw himself walking on a third pathway: Thermodynamics as a generalized Mechanics, as a theory of transformations in a wide sense.

“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.”³⁴

According to Duhem, 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 shape had been outlined by Clausius and “improved” by Massieu, Gibbs and Helmholtz: their efforts had given Thermodynamics “analytic features” similar to Lagrange’s Mechanics. That similarity assured Duhem that, at the theoretical level, his attempt was in continuity with the tradition of physics rather than in competition with it. Nevertheless, at the meta-theoretical level, an interesting discontinuity appeared. Only a carefully distinction between the two traditions emerged in the history of Mechanics allows us to understand Duhem’s design of a generalised Mechanics/Thermodynamics. His design can be looked upon as a reduction of physics to the language of Analytic Mechanics, but, at the same time, as an anti-reductionist design, wherein the widening of the scope of that language was at stake. We could definitely say that Duhem opposed a short-sighted mechanical world-view.

³³ Duhem 1894a, pp. 284-5.

³⁴ Duhem 1894a, p. 285.

“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 physique 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.”³⁵

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”.

³⁵ Duhem 1894a, p. 285.

11. A new “chemical mechanics”

In the meanwhile, early in the in 1890s, Duhem had undertaken another theoretical pathway: it was apparently 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. Three issues were at stake: the attempt at unifying physics and chemistry, the role of Thermodynamics in that unification, and the already outlined design of a generalized physics, which should have managed to describe every kind of material transformation. These issues were mutually intertwined: could the design of a physics of generalized “motions” not entail some sort of unification between physics and chemistry? In the first lines of the book Duhem published in 1893, *Introduction à la mécanique chimique*, he pointed out experimental and theoretical advancements of chemistry in the last two decades. He mentioned, on the one hand, the experimental researches on dissociations, and, on the other hand, the “theoretical developments of thermodynamics”.¹

In accordance with a typical meta-theoretical attitude, which was one of the hallmarks of his scientific practice, Duhem put forward a historical rather than “logical” outline of chemistry in the last century. He deployed the scientific achievements in their chronological order: “the content of a physical law” could have been better appreciated keeping the reader in contact with both the “efforts” required and the “mistakes” dodged for attaining it.

The key-concepts of the history of “chemical mechanics” revolved around 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 wherein Duhem was writing, the role of temperature was given prominence: an

¹ Duhem 1893b, p. v.

“exothermic compound should undergo an increasing dissociation”, as well as an “endothermic compound should be more easily formed” when temperature rises.²

In the first chapter of the book, the historical review focussed on the relationship between chemistry and physics, in particular on the relationship between the chemical key-concept of “affinity” and the physical key-concept of “cohesion”. Berthollet was credited by Duhem with having been the first to have “heralded the possibility” of a “chemical Mechanics” based on the same general “principles” of Newton’s “celestial Mechanics” and Laplace and Poisson’s “physical Mechanics”. Duhem traced back the conceptual root of that commitment to Newton’s famous XXXI *Query* to be found at the end of his *Opticks*. There the grand savant had envisaged short-range forces beside the long-range universal gravitation. Duhem translated Newton’s view into a mathematical law of the kind

$$F = m m' \left[\frac{K}{r^2} + f(r) \right],$$

wherein “the term $K \frac{m m'}{r^2}$ represents *Newtonian attraction*” and the second term $m m' f(r)$ represents “what is named *molecular attraction*”.³

Duhem emphasised two main features of Berthollet’s theory: first, the explanation of “changes of state” taking place in matter in term of molecular attractions. Second, but more important in Duhem perspective, the attempt at giving a unified explanation for both “changes of physical states like fusion, vaporisation, ...” and “chemical phenomena in the strict sense”. The label “affinity” could encompass both of them. Although Duhem did not trust in the specific mechanical models Laplace and Poisson had put forward, he shared, at least in general terms, Berthollet’s meta-theoretical expectation that “more the principles stemming from the chemical theory will be general, more they will look like those of mechanics”.⁴

² Duhem 1893b, pp. vi-vii.

³ Duhem 1893b, pp. 2 and 8. Duhem made reference, in particular, to Berthollet’s 1803 *Essai de statique chimique*. Apart from the

⁴ Duhem 1893b, pp. 9 and 11. The last quotation was excerpted by Berthollet 1803, p. 2. It is worth comparing that passage with a more cautious passage of Duhem himself: “Mais, cette nature des actions moléculaires nous est à peu

If the first chapter let the first two characters of Duhem’s historical reconstruction emerge, namely chemistry and mechanics, the third character, namely the theories of heat, appeared on the stage in the second chapter. Duhem credited Lavoisier and Laplace with having been the first to leave aside the various “philosophical ideas of scholars on the nature of caloric”, because “the physical consequences drawn from them are the same”. The distinction between “free caloric” and “latent caloric” did not depend on the different representations of caloric. In the course of the nineteenth century, there had been a first stage, wherein heat had been assumed to undergo some kind of conservation over time: in particular, in a closed cycle, its value should have not changed. It had been Clausius in 1850 to change the view, and put heat into a different perspective. In the general equation

$$EQ = \tau + \sum \frac{mv^2}{2} - \sum \frac{mv'^2}{2} + E(U_1 - U_2),$$

the first term on the right-hand side represented “the work done by external forces”, followed by the difference between initial and final “living force”. The third term, which W. Thomson would have subsequently named “internal energy”, was assumed to have the property “attributed to heat by the ancient physicists”: it had to depend only on the initial and final state of the transformation. This was “the radical difference between the modern theory of heat and the ancient theory of caloric”.⁵

The third chapter started from the theoretical link between chemistry and the theory of heat put forward in the last decades of the eighteenth century, and went on with the modifications undergone by that ancient theory. Duhem theoretical design of a generalized physics, or a physics of generalized “motions”, had to unify mechanics, thermodynamics and chemistry. He was looking for traces and clues of that possibility of unification in the history of science. The ancient theory had assumed that

près inconnue ; c’est donc l’observation seule, et non l’application, par voie de déduction, des lois de la mécanique rationnelle, qui doit nous révéler les lois de la mécanique chimique. Toutefois, il est à prévoir que ces lois, une fois établies par l’expérience, s’offriront à nous sous une forme qui rappellera les principes de la mécanique rationnelle, dont, logiquement elles sont conséquences.” (Duhem 1893b, p. 10) It seems that, at that stage, Duhem had more confidence in “observations” than in “deductions”.

⁵ Duhem 1893b, pp. 12-7. Duhem specified that the term “living force” dealt only with “the living force of *sensible* motions”, namely macroscopic motions. In no way could it be associated to “the living force of the hypothetical motions by which many physicists explain heat”. (See *Ibidem*, p. 16, footnote 1)

atmospheres of caloric surrounded molecules of ordinary matter, because caloric attracted matter. The atmospheres, on the contrary, would have repelled with 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 spreading out of part of latent caloric”. The victory of thermal repulsion on material attraction would have given place to decompositions: “the amount of latent caloric would grow at the expense of 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 some kind of power.⁶

Once again, Duhem credited Berthollet with having modified the ancient view, calling into play the superposition of physical cohesion and chemical affinity. In other words, *chemical* processes like combination and decomposition could be accompanied by physical processes like contraction and dilatation. Since both chemical and physical processes involved heat and transfers of heat, their superposition could change the increase or decrease of heat expected from the point of view of purely chemical processes. According to Duhem’s translation of Berthollet’s theory, the identification of compositions with exothermic processes was suitable “only for energetic compositions”. The more sophisticated theory could account for “various experiences” involving oxygen and nitrogen, and their combination into or decomposition from nitrogen protoxide. In the process of decomposition, for instance, a given amount of heat was sent out. The emerging oxygen was supposed to be in a “peculiar allotropic state, formed against the forces of cohesion of oxygen itself”, and therefore intrinsically unstable. The re-establishment of the ordinary state had to involve an outflow of heat. In some way, the internal cohesion of oxygen must be destroyed by a given amount of heat, in order to let it undergo the affinity with nitrogen. From the macroscopic point of view, the dismantled cohesion of oxygen had to correspond to a change of volume: actually, the volume of nitrogen protoxide is double the volume of free oxygen.⁷

In Duhem historical reconstruction, Clausius’ theory represented a re-interpretation of the ancient “antagonism between molecular attraction and heat”. The amount of heat

⁶ Duhem 1893b, pp. 28-9.

⁷ Duhem 1893b, pp. 19-24

entering a body could trigger off three different processes: an increase of “free heat” or temperature, macroscopic or external work, and microscopic work done by “molecular forces”. In more ancient words, the last two terms would correspond to the increase of “latent caloric”. Clausius’ internal energy U was nothing else but the sum of “free heat” H and $W=w/E$, “the ratio between the potential of molecular actions and the mechanical equivalent of heat”: $U = H + W$. In other words, or in a mechanical perspective, $E(U_1 - U_2)$ was “the work done by internal forces”.⁸

At that theoretical stage, when the sum of internal and external work was positive, the transformation could actually occur. In the case of negligible variations of macroscopic living force, this means that

$$\mathcal{T} + E(U_1 - U_2) > 0, \text{ and therefore } EQ > 0.^9$$

The remaining part of the fourth chapter was devoted to criticize this theory, or Berthelot’s theory, which could not attain a satisfactory generality. It is worth mentioning that, at that time, Marcelin Berthelot was perhaps the most authoritative scientist of the Third French Republic. The fact is that the recent alliance between physics and chemistry was put in danger by the existence of simple phenomena which Duhem qualified as “merely physical”. Ice melts, water vaporises, and a salt dissolves in a solution, “even though these phenomena absorb heat”. In the “second stage of this history”, the first way out consisted in distinguishing “*chemical* affinities from *physical* affinities”. The fact is that thermodynamics required a sort of symmetry between chemistry and physics: from the point of view of Duhem’s design of unification, there was “nothing more arbitrary than this distinction between chemical and physical forces”.¹⁰

⁸ Duhem 1893b, pp. 26 and 29.

⁹ See Duhem 1893b, p. 35: “*Pour qu’une réaction chimique puisse se produire à une température déterminée, il faut qu’elle entraîne un dégagement de chaleur.*”

Si nous appliquons des considérations analogues au principe des vitesses virtuelles, nous voyons sans aucune peine que celui-ci nous donne la proposition suivante :

Prenons un système dans un certain état chimique ; si toute réaction virtuelle, produite à partir de cet état, entraîne un phénomène thermique nul ou une absorption de chaleur, le système est en équilibre chimique.

¹⁰ Duhem 1893b, pp. 52, 56 and 58.

He credited Sainte-Claire Deville with having restored the unity between physics and chemistry: he had paid attention “on phenomena which occur at temperature of 1000 or 2000 degrees”. In such conditions, we can observe many reactions occurring “with absorption of heat”, without any kind of chemical or physical compensation.¹¹ An example was offered by reactions involving oxygen, hydrogen and water.

“Ainsi, lorsqu’on se donne les conditions physiques d’une expérience, la température et la pression, ces conditions déterminent une certaine composition qui assure l’équilibre du mélange hydrogène, oxygène, vapeur d’eau. Lorsque l’oxygène et l’hydrogène sont portés à cette température, il ne se combinent pas intégralement : la combinaison s’arrête au moment où l’équilibre est atteint. Lorsque la vapeur d’eau est portée à cette température, elle ne se décompose pas totalement ; sa dissociation s’arrête lorsque l’équilibre est atteint. A une température donnée, selon la valeur de la pression et la composition du mélange, on peut observer aussi bien la combinaison de l’oxygène et de l’hydrogène, phénomène qui dégage de la chaleur, que la décomposition de l’eau, phénomène qui absorbe de la chaleur. L’état limite vers lequel, en toutes circonstances, tend le système, n’est pas l’état dont la formation dégagerait le plus de chaleur, c’est à dire l’état où l’oxygène et l’hydrogène seraient intégralement combinés.”¹²

Duhem mentioned other “experiences” performed at “high temperature”: they had shown that “exothermal compounds split, whereas endothermic compounds set up“. In those processes Sainte-Claire Deville had emphasised the strong analogy between “the mechanism of chemical reactions and the mechanism of physical changes of state”.¹³

The sixth chapter ended with some pages devoted to Berthelot, who upheld the old thermo-chemistry, and opposed Sainte-Claire Deville’s new approach. Two short chapters were then devoted by Duhem to the “kinetic theory of gases put forward by Krönig and Claudius, and perfected by Boltzmann and Maxwell”. The “kinetic” theory and the theory of “molecular attraction” stemmed from the same attitude towards

¹¹ Duhem 1893b, p. 68.

¹² Duhem 1893b, p. 69.

¹³ Duhem 1893b, pp. 74-5.

physics, which consisted of starting from some hypotheses on the hidden structure of matter and its transformations. An invisible world, described by specific microscopic mechanical models had to explain those macroscopic effects “appreciated by our senses”.¹⁴ 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 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 haute le mercure du thermomètre ? Pourquoi chercher à se figurer les changements d’état comme des déplacements, des juxtaposition de molécules, des variation 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 ?”¹⁵

He would have turned upside down the “method” or the “ideal” of mechanical models. He suggested giving up the two pillars of that method, the first being theoretical, and the second meta-theoretical: a set of “few, simple mechanical hypotheses” and the belief that they are “real *explanations*”. His method did not aim at “*explaining* the phenomena but *classing* them”.¹⁶

¹⁴ Duhem 1893b, pp. 81 e 87. 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)

¹⁵ Duhem 1893b, p. 88.

¹⁶ Duhem 1893b, p. 89.

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

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \dots + \frac{Q_n}{T_n} + S_b - S_a > 0 \quad \text{or} \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \dots + \frac{Q_n}{T_n} = S_a - S_b + P,$$

where the always positive quantity P corresponded to Clausius’ “uncompensated work”.¹⁷

According to the Principle, an isolated physical system is in equilibrium “if all possible transformations cannot increase its entropy”. Duhem stressed that the Principle is universal, and every design of “chemical mechanics” must take it into account. In the case of isothermal transformations, the last equation can be written as

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

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

$$\vartheta = ET(S_a - S_b) \quad \text{and} \quad \tau = ETP$$

could be interpreted as “*compensated work*” and “*uncompensated work*”. It seemed to Duhem that the second Principle could restore the symmetry between physics and

¹⁷ Duhem 1893b, pp. 93, 96 and 100.

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.¹⁸

The analogy could be strengthened by the recourse to thermodynamic potentials. In fact, if

$$\tau = EQ - ET(S_a - S_b), \text{ and } EQ = \mathfrak{T} + E(U_a - U_b),$$

then the uncompensated work could be written as

$$\tau = \mathfrak{T} + E(U_a - U_b) - ET(S_a - S_b) = E(U_a - TS_a) - E(U_b - TS_b) + \mathfrak{T}.$$

$$\text{Since } F = E(U - TS),$$

the uncompensated work became

$$\tau = (F_a - F_b) + \mathfrak{T}.$$

It seemed “natural” to Duhem that the term $(F_a - F_b)$ received the name of “*internal uncompensated work*”.¹⁹

He stressed the *structural* analogy between physics and thermodynamics as an intermediate stage, in order to state a structural analogy between mechanics and chemistry. If the external forces could be derived by a potential Ω , the uncompensated work could be written as the difference between initial and final values of a “total thermodynamic potential” $\Phi = F + \Omega$:

$$\tau = (F_a + \Omega_a) - (F_b + \Omega_b) \text{ or } \tau = \Phi_a - \Phi_b.$$

¹⁸ Duhem 1893b, pp. 104 and 106-8.

¹⁹ Duhem 1893, pp. 108-10.

According to Duhem, at this stage, the analogy between analytic mechanics and thermodynamics, as well as between analytic mechanics and chemistry could be considered actually accomplished.

“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 un valeur minima.*

L’analogie entre la statique chimique et la statique mécanique est complète.”²⁰

He then showed that the *structural* analogy between analytic mechanics and thermodynamics could be exploited right to the end, at least for isothermal transformations. If the system is looked upon as “a source of work” $\mathfrak{T}' = -\mathfrak{T}$,

$$\mathfrak{T}' = (F_a - F_b) - \tau,$$

and the work done by the system is always less than “the decrease of the internal thermodynamic potential”, because “ τ is positive”. He remarked that the analytical-mechanical interpretation of the second Principle was consistent with Maxwell and Helmholtz’s lexical choices of “available energy” and “*freie Energie*” respectively. He thought that his re-interpretation could “shed light on the close analogy between the laws of thermodynamics and the laws of statics” better than “Gibbs, Maxwell and von Helmholtz methods”. The old “thermo-chemistry” should have given way to a “chemical mechanics based on thermodynamics”.²¹

²⁰ Duhem 1893, pp. 112-3. As already stressed, that *structural* analogy was quite different from the contemporary attempts at transferring specific *mechanical models* from mechanics to thermodynamics and chemistry.

²¹ Duhem 1893, 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 a battery connected to an electric circuit, whose resistances are r and R respectively, heat sent out by “chemical reactions taking place inside battery in unit time” was

$$Q = \frac{1}{E}(r+R)J^2,$$

where J is both the amount of electric current in the wire, and the amount of electricity travelling through the battery in unit time. From Faraday’s law, if L is the heat sent out in the chemical reaction corresponding to the “the passage of an amount of unit electricity”, we also have

$$Q = LJ \quad \text{and therefore} \quad \frac{1}{E}(r+R)J = L.$$

According to Ohm’s first law, we could write

$$\mathcal{E} = (r+R)J \quad \text{and therefore} \quad \mathcal{E} = EL.$$

The hypothesis corresponding to the equation $Q = LJ$ was expressed by Duhem in the following way: “*in a battery, voltaic heat equates chemical heat*”.²²

Nevertheless, this theoretical result, put forward by Joule, Helmholtz and E. Becquerel, seemed falsified by experiments subsequently performed by other scientists: Favre, Hirn, Raoulr, Edlund, ... In some experiments, as Duhem summarized,

²² Duhem 1893b, pp. 118-20. It is worth mentioning that the identifications 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 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 elastic medium stemmed from a conceptual trend quite far from Duhem *structural* analogies based on analytic 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.

“chemical heat is greater than voltaic heat” whereas, in other experiments, on the contrary, “chemical heat is smaller than voltaic 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*”. More critical appeared the opposite case, when voltaic heat was greater than chemical heat. How could a positive part of the total heat, namely its uncompensated component, be greater than the whole? The fact is that – Duhem remarked – “chemical uncompensated heat is positive when the reaction taking place inside battery occur by itself”, in some spontaneous way. In other cases, the uncompensated heat could be zero or negative. He did not explain the query in detail, but we can make reference to a thermal engine operating in a reversed way. In a thermal engine, the dissipated heat is assumed to be positive; when the engine is forced to operate as a refrigerating engine, the uncompensated heat must be negative.²³

What differentiated Duhem’s “theory of the thermodynamic potential” from the old “thermo-chemistry” could be summarized as follows: the former “replace the uncompensated heat to total heat”. In particular – Duhem specified - only 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 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”, when chemical reactions are particularly “violent”.²⁴

The last chapter dealt with a different query, emerging from the already mentioned experiments performed at high temperature: the question of “false equilibrium”. What is a “false” equilibrium? Thermodynamics forbids some transformations, and nobody has ever observed such kind of forbidden transformations. On the contrary, when some transformation is foretold by the theory, sometimes it does not happen. In some way,

²³ Duhem 1893b, pp. 123 and 131. The analogy between the voltaic cell and the thermal engine was put forward by Duhem himself in order to justify the fact that the heat developed in the chemical reaction could not be totally transformed into electric energy. See *Ibidem*, p. 121: “On peut donc espérer, en prenant des piles de résistance intérieure extrêmement faible, de transformer en travail toute la chaleur que la réaction chimique est susceptible de produire. On sait, au contraire, que si l’on employait cette réaction chimique à échauffer le foyer d’une machine à feu, une partie seulement de la chaleur dégagée par cette réaction serait transformée en travail. La proposition énoncée par M. Joule, par M. H. von Helmholtz, par Edm. Becquerel, établit donc entre les électromoteurs et les machines à feu une différence, toute à l’avantage des premiers, qui amènerait nécessairement l’industrie à préférer les électromoteurs aux machines à feu.”

²⁴ Duhem 1893b, pp. 137 and 139.

the system keeps itself in equilibrium even when it should not: that equilibrium is Duhem “false” equilibrium. In other words, when “the system should be in equilibrium, it actually stay in equilibrium”, but it can stay in equilibrium “even when, according to the theory, it should not”. The former was called “true equilibrium”, while the latter “false equilibrium”.²⁵

Duhem pointed out that the Principles of thermodynamics “are exact”, but an auxiliary hypothesis which scientists had made use of had prevented them from understanding those “false” equilibriums. In order to explain that hidden hypothesis, Duhem took into account a certain amount M of water at 100°C under atmospheric pressure. Let us imagine water in two different physical states: as a cup of water, and as a huge collection of infinitesimal drops scattered throughout space. In the latter state, water has an “internal thermodynamic potential” $F = M\varphi$, where φ depends only on water temperature and density. In the former, not only the potential depends on temperature and density, but also on “the order of different elements”, and therefore on the “shape” of M . This contribution could be summarized by the term Ψ in the expression $F = M\varphi + \Psi$. Duhem pointed out that the underestimation of the additional term was not justified in general, even though “the classical theories of hydrostatic, hydrodynamic and elasticity” just did it.²⁶

Following the track of Gibbs, Duhem generalized the model to “a system containing a certain number of homogeneous bodies”: he labelled $M, M', \dots$ be their masses, and $S, S', \dots$ the surfaces of contact with each other or with the external bodies. He assumed a thermodynamic potential of the kind

$$F = M\varphi + M'\varphi' + \dots + AS + A'S' + \dots,$$

wherein “ φ depends only on the state of the mass M , φ' on the state of the mass M' ...”, and “ A depends on the nature of bodies separated by $S, \dots$ ”. The terms of the first

²⁵ Duhem 1893b, pp. 157-9. In the 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 croître graduellement sa température, nous n’y déterminerons tout d’abord aucune réaction chimique ; puis, tiut à coup, lorsque la température atteindra environ $+500^{\circ}\text{C}$, une partie du mélange gazeux passera avec explosion à l’état de vapeur d’eau.”

²⁶ Duhem 1893b, pp. 162-4.

kind in the right side of the above equation depend on the cube of the linear dimensions of every body. The terms of the second kind depend on the square of their linear dimensions. Simple geometrical considerations followed: for dimensions greater than a given unitary dimension, the former overwhelm the latter, but for dimension smaller than the given unity, the former are overwhelmed by the latter.²⁷

What are the consequences of that apparently line of reasoning? In the case of water vapourisation, when a mass of water is in contact with a mass of steam, if we are dealing with great masses, only terms of the first kind are at stake, and “the classic theory of vaporisation” will follow. In other words, “liquid and steam are in equilibrium only at a specific pressure”, namely “the tension of saturated steam”; for smaller pressures, the liquid vaporise, and for greater pressures, steam condense. Quite different should be the case of “a small bubble of steam surrounded by liquid”: the terms of the second kind will become much greater, leading to “conclusions” quite different from the other case.

“Pour qu’une bulle de vapeur pousse croître au dépens du liquide qui l’environne, il ne suffit pas que la pression en un point voisin de cette bulle soit inférieure à la tension de vapeur saturée ; il faut encore que le rayon de la bulle dépasse un certain limite, limite qui dépend d’ailleurs de la température et de la pression ; lorsque le rayon de la bulle est inférieur à cette limite, non seulement la bulle ne peut grossir au dépens du liquide qui l’environne, mais encore la vapeur qu’elle renferme se condense forcément ; la bulle se résorbe.”²⁸

The concept of “false” equilibrium allowed Duhem to interpret another class of phenomena: chemical systems “at a temperature lower than the point of reaction”. When the reaction takes place, it leads the system “to its true equilibrium”; at the same time, “the reaction is accompanied by a powerful release of heat”. We are dealing with an explosion. Cases of this kind are in no way unusual: a mixture of hydrogen and oxygen, or hydrogen and chlorine. When they reach their “true” equilibrium, namely water and muriatic acid, they release a so great amount of heat to trigger an explosion. In Duhem’s theoretical framework, an explosion was therefore a passage “from a state

²⁷ Duhem 1893b, pp. 165-6.

²⁸ Duhem 1893b, p. 168.

of false equilibrium to a state of true equilibrium”, wherein “a remarkable amount of heat” was released. The theory was “fruitful”: it could account for sudden and disruptive events left unexplained by the old theories.²⁹

At the end of this detailed and demanding inquiry into the history of Mechanics, Thermodynamics and Chemistry, Duhem realized how complex was the net of theories inherited by contemporary science. He 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, both the old-fashioned and the more recent ones.

“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.”³⁰

On the other hand, the scientific practice could have not survived without theoretical frameworks, no matter how they were provisional, incomplete and even flawed. This fact explained why scientists had sometime tried to save at any cost a flawed theory when a better theory was not at hand yet.

“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 ; l’amour-propre d’inventeur, l’attachement obstiné aux idées reçues, le respect exagéré de l’autorité sont souvent pour beaucoup dans ces procédés peu logiques ; mais il faut les attribuer surtout au besoin qu’a l’esprit

²⁹ Duhem 1893b, pp. 173-4.

³⁰ Duhem 1893b, p. 176.

humain de grouper tant bien que mal les phénomènes qu'il observe autour de quelque 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."³¹

Meta-theoretical issues were really at stake in the contemporary debate on thermo-chemistry, and physical chemistry in general, even though triggered off by specific theoretical issues like the reliability mechanical models of matter and the role of entropy. In 1894 and 1895 Berthelot faced explicitly the second issue, and Wilhelm Ostwald the first one.

In 1894, Berthelot sent a paper to *Comptes Rendus de l'Académie des Sciences*, dealing with thermo-chemistry, in particular the thermodynamic interpretation of some 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". He stressed that the words "*endothermic*" and "*exothermic*" had been introduced only recently, and in the course of his researches. Provided that there were chemical "combinations realised by release of heat" and "combinations realised by absorption of heat", Berthelot put forward his fundamental issue: the nature of the 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").³²

Among the different kinds of "outsider heat", he listed "external mechanical work", and "purely physical changes of state". These kinds of heat had to be subtracted to "the rough heat", in order to compute "the chemical heat in its strict sense". It was just 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".

³¹ Duhem 1893b, p. 176.

³² 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 : $Q > Q' > Q''$ ³³

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”: rather than deducting “latent heat of fusion, evaporation, and dissociation” from “total heat”, we can deduct “heat not transformable into mechanical work”, whose most component was just “latent heats”. In brief, what he had labelled “*chemical heat*” was “noticeably equivalent to heat transformable into work”.³⁴

Nevertheless, the mathematical equivalence did not convince Berthelot of the conceptual equivalence: he found that the law expressed in terms of entropy had a “more limited” scope, and its previsions were “more obscure”. Some chemical systems had not “computable entropy”: entropy was a physical quantity suitable for “people dealing with computation in the context of mathematical physics”. The intrinsic “discontinuity” of chemical processes did not allow scientists to “... them within the framework of a mathematical approach”. Even in subsequent passages Berthelot insisted on the gap between mathematical algorithms and experimental practice: entropy

³³ Berthelot M. 1894, p. 1381.

³⁴ Berthelot M. 1894, p. 1382.

was “an obscure concept”, and a quantity “disconnected from experience in most cases” and unsuitable for “the interpretation of most chemical phenomena”.³⁵

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 have been abandoned, and “existence and importance” of “previous laws” should not have been “neglected”. In some way, he left the field of specific theoretical explanations, and entered the field of meta-theoretical or epistemological remark. He claimed that “the discoveries of experimental sciences form a continuous chain”, and “the positive facts and relations achieved in Thermo-chemistry today could not be overthrown”. He went on with the same kind of reasoning, and stressed the possibility to improve old theory by means of “new facts and concepts”.³⁶

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 improvement of Thermo-chemistry, he did not say as well. Probably Berthelot chose the meta-theoretical level because he knew that the most conclusive effects of the scientific debate stood on that level. That the feeble link between mathematical physics and thermo-chemistry could be transformed into a fruitful alliance, was believed by Duhem, and was denied by Berthelot.

In a paper sent to *Revue générale des Sciences pures et appliquées* in 1895, Ostwald, then professor of Physical Chemistry at Leipzig University, criticised sharply scientists who believed in “the Mechanics of atoms” as an intellectual “key” for the comprehension of the physical world. To this mechanical world-view, which Ostwald qualified as “physical materialism”, he opposed “a new theory” he labelled “energetics”. Although he claimed that he would have confined himself to “positive science”, namely “exact sciences”, in a subsequent passage he did not manage to restrain from stating that the rejection of a mechanical world-view was an attack to “the general materialistic view”. In general, however, the paper appears as an unmistakable but balanced 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

³⁵ Berthelot M. 1894, pp. 1383 and 1385.

³⁶ Berthelot M. 1894, p. 1392.

discovery of “invariants”, namely physical entities which preserved their values in the course of a physical transformation. He found that the pretension to explaining “all known physical phenomena by means of Mechanics” was “a vain enterprise”. He reminded the reader about the discovery of polarisation in optical phenomena: the mechanical models of aether endowed with some properties of solid bodies, which would have explained the polarisation, were physically inconsistent.³⁷

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 face was represented by the irreversibility of real 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, the energy”, or, better, any difference of energy.³⁸

In Ostwald foundation of physics, energy assumed the role played previously by matter. To anybody who had thought that energy is “an abstraction” whereas “matter is the reality”, he claimed that it was “just the contrary”. According to Ostwald, matter was “a mental creation” put forward in order to “represent what is constant in the transformations”, whereas the material effects of those transformations on our senses was actually linked to the energy. The concept of “mass”, one of the concept stemming from the concept of matter, was nothing more than “*the capacity of kinetic energy*”; the concept of “*impenetrability*”, nothing more than “*energy of volume*”; the “*weight*”, nothing more than “*energy of position*”; eventually “*the chemical properties*”, nothing more than “*chemical energy*”. In brief, matter corresponded to “a set of different

³⁷ Ostwald W. 1895a, p. 953-5.

³⁸ Ostwald W. 1895a, p. 955-7.

energies” whose mutual relationships were submitted to a sole hypothesis: a general law of conservation.³⁹

According to Ostwald, 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”, acting on atoms, “which we cannot see”, 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. This passionate hymn to energy was accompanied by a more sober meta-theoretical attitude towards the 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 mechanic theory” notwithstanding, energetics had 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”.⁴⁰

When we compare Ostwald with Duhem 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. In a brief letter Ostwald sent to the same journal after some weeks as a response to the criticism of the French physicist M. Brillouin, he stressed synthetically the same view put forward in the previous paper. With regard 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 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”.⁴¹ On both theoretical and meta-theoretical levels, we can appreciate the distance between Ostwald and Duhem energetics.

³⁹ Ostwald W. 1895a, pp. 956-7. In order to show that energy was something more palpable than matter, Ostwald asked: “Vous recevez un coup de bâton. Que ressentez-vous, le bâton ou son énergie?” (*Ibidem*, p. 957)

⁴⁰ Ostwald W. 1895a, pp. 957-8.

⁴¹ Ostwald W. 1895b, pp. 1070-1.

12. Looking for a theory of permanent deformations

In 1894 Duhem sent to a Belgian scientific journal a long paper under the title *Sur les déformations permanentes et l'hystérésis*. The following year he sent two other papers under the same title, but with the sub-titles *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”. Duhem devoted some pages, in particular, to criticize the theory M. Brillouin had outlined in 1888 and 1889. 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 led naturally to the exclusion of phenomena like magnetic hysteresis. In this kind of phenomena, “*a continuous series of states of equilibrium is not a reversible transformation*”, and the second Principle of thermodynamics could not be called into play. The only theoretical pillar at disposal was “the principle of equivalence between heat and work”, namely the first Principle of Thermodynamics. At the end of the “Introduction”, Duhem pointed out the limited theoretical grounds he could rely on: the first Principle “is the only principle of thermodynamics we are allowed to apply”.¹

The first chapter is the longest of the paper, and it is also its theoretical core. He started from a simplified physical system defined by a temperature T and a single “normal variable x ”, and applied to it “the classic propositions of thermodynamics”. 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 :

¹ Duhem 1894b, pp. 3 and 7.

$$\mathcal{F} = E(U - TS), \quad (5) \quad EU(x, T) = \mathcal{F}(x, T) - T \frac{\partial \mathcal{F}(x, T)}{\partial T}, \quad \text{and}$$

$$X = \frac{\partial \mathcal{F}(x, T)}{\partial x}.$$

As a consequence,

$$(7) \quad dX = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} dx + \frac{\partial^2 \mathcal{F}(x, T)}{\partial x \partial T} dT.^2$$

Although dealing with irreversible phenomena, Duhem assumed that “a function $\mathcal{F}(x, T)$, which we still call *internal thermodynamic potential*” did exist, and which the “*internal energy*” could be derived from it. As a further hypothesis, equation (7) was replaced by a slightly different one, wherein a new term was added:

$$(8) \quad dX = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} dx + \frac{\partial^2 \mathcal{F}(x, T)}{\partial x \partial T} dT + f(x, T, X)|dx|.$$

The function $f(x, T, X)$ was an unspecified “*uniform and continuous* function of the three variables x, T, X ”. It was just 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 the transformation. At that stage, Duhem confined himself to isothermal transformations, for he was interested mainly in mechanical deformations. Therefore the last equations assumed the simplified form

$$(8^{\text{bis}}) \quad dX = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} dx + f(x, T, X)|dx|.$$

² Duhem 1894b, pp. 7-8.

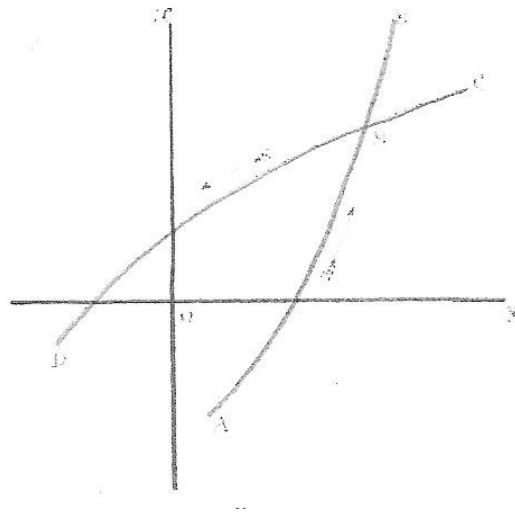
If $x > 0$, when the physical system undergoes some kind of generalized *motion*, the equation gives rise to “the family of ascending curves”:

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

If $x < 0$, when the system *comes back* from the point of view of that generalized *motion*, the equation gives rise to “the family of descending curves”:

$$\frac{dX}{dx} = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} - f(x, T, X).^3$$

Duhem assumed that “for every point M of the plane (X, x) , only an ascending curve and a descending curve are allowed”.



Picture 1 (Duhem 1894b, p. 9)

From the point of view of analytic geometry, the last two equations are nothing else but the reciprocals of the angular coefficients α and β of the tangent lines to ascending and descending curves:

³ Duhem 1894b, pp. 8-10.

$$\frac{1}{\alpha} = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} + f(x, T, X) \quad \text{and} \quad \frac{1}{\beta} = \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} - f(x, T, X).^4$$

Since he could not rely on Carnot's principle for reversible transformations, Duhem was looking for "a new hypothesis". He thought he could rely on the following one: for "states of equilibrium infinitely close to each other, corresponding to a same temperature T of the system",

$$dX dx > 0.$$

From the geometrical point of view, the hypothesis was consistent with the two curves drawn above: "every ascendant curve" goes up from left to right", and "every descendant curve goes down from right to left". From the analytic point of view, it had two consequences:

$$\frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} + f(x, T, X) > 0, \quad \frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} - f(x, T, X) > 0,$$

and therefore

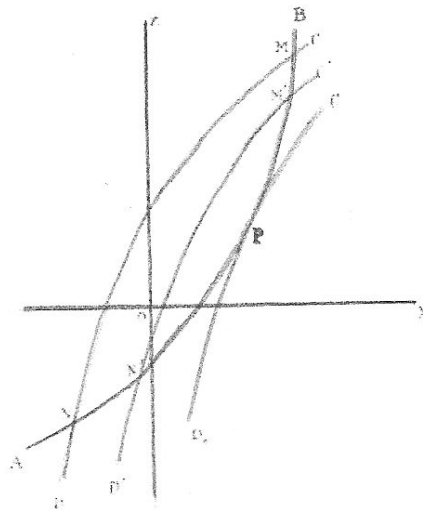
$$\frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2} > 0.$$

He assumed the existence of a new kind of closed cycle, a cycle of hysteresis, consisting of "a descendant 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 cycle. The new

⁴ Duhem 1894b, pp. 9-10.

kind of cycle was, in some way, the fundamental entity of the new thermodynamics of permanent, irreversible transformations.⁵

In a simple closed cycle, on the ascending curve there is a point wherein a curve belonging to the bundle of descending curves is tangent. A similar point can be found on the descending curve of the cycle. Such kinds of points were labelled by Duhem “*natural states*”, and he proceeded to demonstrate that, in every isothermal closed cycle, “*we can find at least two natural states of the system*”.



Picture 2 (Duhem 1894b, p. 14)

Why were they qualified as “natural”? In those point of the graph, $\alpha = \beta$ and therefore

$$f(x, T, X) = 0.$$

In some way, in those points the effects of the new irreversible Mechanics/Thermodynamics are not operating, and ordinary thermodynamics is at stake. The behaviour of the physical system in those states emerges in a clearer way when we show the relationship between the external force and the transformations experienced by the “normal” parameter x . Let us assume that the external force X act

⁵ Duhem 1894b, pp. 11 and 13.

along a given direction and then in the opposite, with the same intensity. From equation (8^{bis}),

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

$$(16) \quad \sum_{k=1}^2 dx_k = - \frac{f(x, T, X)}{\frac{\partial^2 \mathcal{F}(x, T)}{\partial x^2}} \sum_{k=1}^2 |dx_k|. ^6$$

When the sum of applied forces vanishes, the physical system does not return to its initial conditions: it has experienced an irreversible strain $(x_1 - x_0)$. Only if $f(x, T, X) = 0$, the system can dodge an irreversible transformation: only in natural states the system do not suffer permanent transformations.

“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

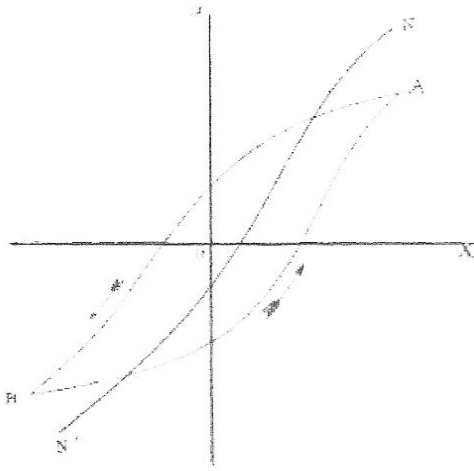
$$x_1 - x_0 = 0.$$

*Une modification infiniment petite, accomplie au voisinage d’un état naturel, n’entraîne 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 ; ...”*⁷

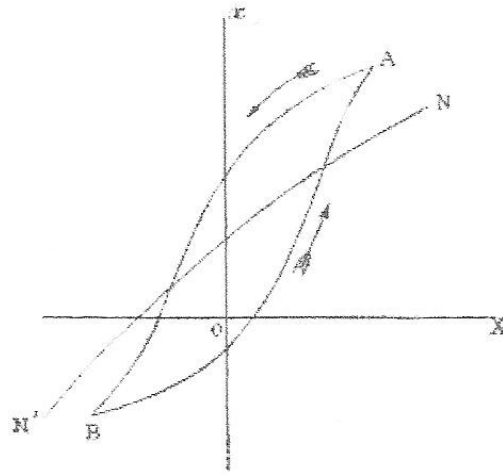
⁶ Duhem 1894b, p. 17. I have slightly modified Duhem’s formalism.

⁷ Duhem 1894b, pp. 17-8.

After a series of long mathematical steps, Duhem showed the existence of two kinds of permanent deformations, corresponding to two slightly different graphs:



Picture 3 (Duhem 1894b, p. 29)



Picture 4 (Duhem 1894b, p. 29)

In spite of the very slight difference in their geometrical representations, systems of the “first category” and systems of the “second category” behaved in a very different way with regard to stability. In order to explain the different behaviour, Duhem choose a physical system swinging “with small amplitude around a fixed point x_0 ”, when temperature undergoes “small variations around a fixed value T_0 ”. He took into account processes more general than purely isothermal ones: it could therefore be $dT \neq 0$. The integration over space of the general equation (8), in the case of “very slow variations” and “very great number of oscillations”, let “infinitely small quantities” vanish, and “a finite value for $\int |dx|$ ” emerge. In other words, after many slow oscillations $dX = 0$ and $dT = 0$, and only two kinds of terms survived:

$$\left[\frac{\partial \mathcal{F}(x_1, T_0)}{\partial x_1} - \frac{\partial \mathcal{F}(x_0, T_0)}{\partial x_0} \right] + \int f(x, T, X) |dx| = 0,$$

wherein x_0 and x_1 are initial and final values of the geometrical parameter. After other mathematical steps (and some misprint) Duhem found that the first kind of system approaches “the natural state (ξ, X_0, T_0) corresponding to the temperature T_0 and the external action X_0 ”. The system is therefore stable. On the contrary, systems of the second kind are not stable: they “change endlessly” when submitted to “an external force and a temperature THEREABOUTS constant”. This difference involved even “natural states”: they were “stable states for system of the first category” but “unstable states for the systems of the second category”.⁸

Duhem made use of the general equation (8) 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 mathematical represented in an abstract *plane* (X, x) , thermal processes like quenching could better be represented in an abstract *plane* (T, x) .⁹

A slightly different approach was required in the case of magnetic permanent deformations, namely the phenomena known as “magnetic hysteresis”. The concept of “external action” did not suit “a magnetic element placed inside a magnet”. Differently from the mechanical case, there was both a “magnetism” acting on the element as well as on the “surrounding magnets”, and the “magnetic intensity” or “the magnetic state” or “the state of magnetisation” of the given element. The first magnetic action $\mathbf{H}$ could be derived by a “potential function $\mathcal{V}$ ”, according to the law

$$\mathbf{H} = \left(-\frac{\partial \mathcal{V}}{\partial x}, -\frac{\partial \mathcal{V}}{\partial y}, -\frac{\partial \mathcal{V}}{\partial z} \right),$$

⁸ Duhem 1894b, pp. 33-4 and 37-8.

⁹ Duhem 1894b, pp. 38 and 44-5.

and could play the role of the external force X . The second magnetic action $\mathfrak{M}$, in the specific case of “perfectly *soft* bodies”, could be put in a simple, even though *recursive*, relationship with H :

$$\mathfrak{M} = F(\mathfrak{M}, T)H,$$

wherein the function $\mathfrak{M} = F(\mathfrak{M}, T)H$ was “the magnetising function”. In the theoretical framework of Duhem’s theory, $\mathfrak{M}$ played the role of a “normal variable”. Both H and $\mathfrak{M}$ 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 H was assumed to have “a constant direction”, and the magnetisation $\mathfrak{M}$ 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”.¹⁰

The formal analogy between mechanical and magnetic processes led Duhem to marshal a series of equations leading to his “*fundamental equation of magnetic hysteresis*”. From

$$H = \frac{\mathfrak{M}}{F(\mathfrak{M}, T)}$$

he derived the expression for dH :

$$dH = \left[\frac{1}{F(\mathfrak{M}, T)} - \frac{\mathfrak{M}}{[F(\mathfrak{M}, T)]^2} \frac{\partial F(\mathfrak{M}, T)}{\partial T} \right] d\mathfrak{M} - \frac{\mathfrak{M}}{[F(\mathfrak{M}, T)]^2} \frac{\partial F(\mathfrak{M}, T)}{\partial T} dT.$$

If we formally put

¹⁰ Duhem 1894b, pp. 51-3.

$$\begin{cases} G(\mathfrak{M}, T) = \frac{1}{F(\mathfrak{M}, T)} - \frac{\mathfrak{M}}{[F(\mathfrak{M}, T)]^2} \frac{\partial F(\mathfrak{M}, T)}{\partial T} \\ g(\mathfrak{M}, T) = -\frac{\mathfrak{M}}{[F(\mathfrak{M}, T)]^2} \frac{\partial F(\mathfrak{M}, T)}{\partial T} \end{cases}$$

then we have an equation corresponding formally to (7):

$$(52) \quad dH = G(\mathfrak{M}, T) d\mathfrak{M} + g(\mathfrak{M}, T) dT.$$

As Duhem himself specified, this equation could only represent “magnetic bodies which are perfectly soft”. When we are dealing with bodies “endowed with a coercive force”, the equation must be generalized in accordance to (8):

$$(53) \quad dH = G(\mathfrak{M}, T) d\mathfrak{M} + g(\mathfrak{M}, T) dT + f(\mathfrak{M}, H, T) |d\mathfrak{M}|.$$

The structure of equation (53) is similar to the structure of equation (8), but the content of the differential coefficients in the two right sides are quite different. Moreover, in this case, Duhem did not pursue the physical/mathematical approach in terms of internal thermodynamic potential. It was just “the experience” to show that “a magnetised body is a system of the first category”.¹¹

Duhem was aware of the tentative and provisional nature of his theory. It could account for “the most important experimental outcomes”, and reduced the description of a magnetic body “to the experimental specification of the two functions $F(\mathfrak{M}, T)$ and $f(\mathfrak{M}, H, T)$ ”. On the other hand, the theory lacked in generality: it could not account, for instance, for “the influence of mechanical actions or elastic deformations on magnetisation”. A more general theory, “depending on more than one normal variable”,

¹¹ Duhem 1894b, pp. 53 and 59.

was required: among the expected “great difficulties”, Duhem mentioned the impossibility of relying on simple “geometrical representations”.¹²

The second paper Duhem devoted to permanent deformations deals with a specific chemical-physical phenomenon: “the permanent modifications sulphur experiences under the influence of heat”. Chemists knew that, when heated, “soluble sulphur in carbon sulphide is transformed in part ... into insoluble sulphur”. Liquid sulphur is, in general, “a mixture of two substances ..., one being the allotropic state of the other”: it can solidify both “in the octahedral state and in the prismatic state”. Solid sulphur also “is not a well definite substance”, but a mixture of “different sulphurs” in variable proportions.¹³ Temperature and concentration were critical parameters for the transformations involving the two kinds of sulphur.

“Le soufre octaédrique peut se transformer en soufre prismatique au contact d’une parcelle de soufre prismatique ; il suffit, pour cela, que la température soit supérieure à une certaine limite $Z(x)$, variable avec la concentration x , mais toujours supérieure à $97,2^\circ$. Ce point de transformation s’élève lorsque la concentration x augmente.”¹⁴

Duhem was dealing here with phenomena placed outside the explanatory scope of ordinary mechanics, thermodynamics and chemistry. He saw an analogy between the change of physical state of sulphur and the process of quenching: both of them were transformations occurring “at variable temperature under a constant external action”. For the moment however the approach was quite formal, since he introduced two “normal parameters”: 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 one and only force which the system was submitted to. Under a constant temperature, the conditions of equilibrium are

¹² Duhem 1894b, p. 61.

¹³ Duhem 1895a, pp. 4 and 54. Liquid sulphur had a very peculiar behaviour with regard temperature. See p. 38: “Si, après avoir fondu du soufre, on porte le liquide à des températures variables, pour le refroidir ensuite et en déterminer la solidification ..., on trouve que la température de solidification, au lieu d’être fixe, comme pour la plupart des liquides, dépend des températures par lesquelles on a fait passer le soufre liquide : ...”

¹⁴ Duhem 1895b, pp. 70-1.

$$\frac{\partial \mathcal{F}(x, v, T)}{\partial v} = \Pi \quad \text{and} \quad \frac{\partial \mathcal{F}(x, v, T)}{\partial x} = 0.$$

The differentiation of the last equation offers

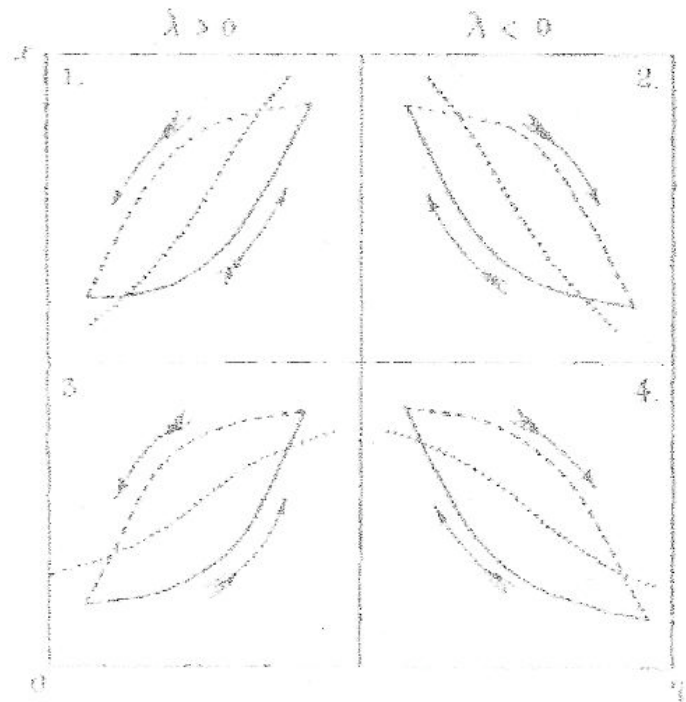
$$\frac{\partial^2 \mathcal{F}(x, v, T)}{\partial x \partial v} \delta v + \frac{\partial^2 \mathcal{F}(x, v, T)}{\partial x \partial T} \delta T + \frac{\partial^2 \mathcal{F}(x, v, T)}{\partial^2 x} \delta x = 0.$$

This is the equation which Duhem generalised in order to take into account permanent transformations:

$$\frac{\partial^2 \mathcal{F}(x, v, T)}{\partial x \partial v} \delta v + \frac{\partial^2 \mathcal{F}(x, v, T)}{\partial x \partial T} \delta T + \frac{\partial^2 \mathcal{F}(x, v, T)}{\partial^2 x} \delta x + f(x, v, \Pi, T) |\delta x| = 0.^{15}$$

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 the three binary parameters: the “category”, the direction of the path, and the sign of the heat exchanged.

¹⁵ Duhem 1895a, pp. 4-5 and 8-9.



Picture 5 (Duhem 1895a, p. 36)

Duhem showed that if “Clausius’ inequality”

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

had been assumed as a further hypothesis, the eight families of closed cycles would have become four. In particular, endothermic cycles could only be clockwise, and exothermal ones only anticlockwise.¹⁶

In the following chapters, Duhem developed a detailed experimental analysis, and tried to compare his graphs with experimental data. But it was only in the third paper that he put forward a general theory of permanent transformations. In the “Introduction”, he briefly recollected the specific processes 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”,

¹⁶ Duhem 1895a, pp. 27, 33 and 35-6. As Duhem remarked, an irreversible cycle does not fulfil the conditions required by the demonstration of “Clausius’ inequality”. (See *Ibidem*, p. 35)

which he would have developed in three different directions: systems described “by any number of normal parameters”, simultaneous variations of temperature and external actions, and the theoretical integration with the theory outlined in the *Commentaire aux principes de la thermodynamique*.¹⁷

Duhem tried to further generalize the generalized Mechanics/Thermodynamics he had put forward in his 1891 “Sur les équations générales de la Thermodynamique”, and in the subsequent three-part *Commentaire*. First of all he reminded the reader that transformations could be “workable” or “purely virtual”: workable transformations split into “reversible” and “not reversible”. Then he summarise the theory put forward on reversible transformations in the *Commentaire*. He had started from the choice of the “normal” parameters $\alpha, \beta, \dots, \nu$, which, together with temperature the T specified “the state of the system”. $A, B, \dots, N$ were “the external actions” associated to those parameters. An “internal thermodynamic potential” $\mathcal{F}(\alpha, \beta, \dots, \nu, T)$ could be defined as “uniform and continuous function”, and the internal energy $U(\alpha, \beta, \dots, \nu, T)$ could be defined in terms of $\mathcal{F}(\alpha, \beta, \dots, \nu, T)$:

$$EU(\alpha, \beta, \dots, \nu, T) = \mathcal{F}(\alpha, \beta, \dots, \nu, T) - T \frac{\partial}{\partial T} \mathcal{F}(\alpha, \beta, \dots, \nu, T).$$

The equilibrium of the system was assured by necessary and sufficient conditions:

$$\begin{aligned} A &= \frac{\partial}{\partial \alpha} \mathcal{F}(\alpha, \beta, \dots, \nu, T) \\ B &= \frac{\partial}{\partial \beta} \mathcal{F}(\alpha, \beta, \dots, \nu, T) \quad .^{18} \\ &\dots \dots \\ N &= \frac{\partial}{\partial \nu} \mathcal{F}(\alpha, \beta, \dots, \nu, T) \end{aligned}$$

¹⁷ Duhem 1895b, p. 4.

¹⁸ Duhem 1895b, pp. 6-7.

The thermodynamics of reversible processes had a too narrow scope, and processes of permanent deformations called into play “a wider, more comprehensive thermodynamics”. On the other hand, the former should have been looked upon “as a specific instance” of the latter. In the set of Lagrangian parameters $\alpha, \beta, \dots, \nu$ he defined two subset $\alpha, \beta, \dots, \lambda$ and $\mu, \dots, \nu$. To the second subset he associated a series of *old* conditions of equilibrium

$$(III.4) \quad \left\{ \begin{array}{l} M = \frac{\partial \mathcal{F}}{\partial \mu} \\ \dots \\ N = \frac{\partial \mathcal{F}}{\partial \nu} \end{array} \right. \quad \text{or} \quad \left\{ \begin{array}{l} dM = \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \mu} d\alpha + \dots + \frac{\partial^2 \mathcal{F}}{\partial^2 \mu} d\mu + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \mu} d\nu \\ \dots \\ dN = \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \nu} d\alpha + \dots + \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \nu} d\mu + \dots + \frac{\partial^2 \mathcal{F}}{\partial^2 \nu} d\nu \end{array} \right. .$$

Duhem specified that the conditions were necessary but not sufficient. To the first subset of parameters he associated a series of *new* conditions of equilibrium

$$(III.5) \quad \left\{ \begin{array}{l} dA = \frac{\partial^2 \mathcal{F}}{\partial \alpha^2} d\alpha + \dots + \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial \alpha} d\lambda + \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \alpha} d\mu + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \alpha} d\nu + \frac{\partial^2 \mathcal{F}}{\partial T \partial \alpha} dT + g_\alpha(\alpha, \dots, \nu, T) |d\alpha| \\ \dots \\ dL = \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \lambda} d\alpha + \dots + \frac{\partial^2 \mathcal{F}}{\partial \lambda^2} d\lambda + \frac{\partial^2 \mathcal{F}}{\partial \mu \partial \lambda} d\mu + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \lambda} d\nu + \frac{\partial^2 \mathcal{F}}{\partial T \partial \lambda} dT + g_\lambda(\alpha, \dots, \nu, T) |d\lambda| \end{array} \right.$$

Only these parameters were affected by irreversible effects: he loaded the burden of irreversibility exclusively on the shoulders of $\alpha, \beta, \dots, \lambda$. With regard to the function $\mathcal{F}(\alpha, \beta, \dots, \nu, T)$, he specified that its existence depended on the choice of the parameters $\alpha, \beta, \dots, \nu$: for the moment he confined himself to state that they had to be “CONVENIENTLY CHOSEN”.¹⁹

¹⁹ Duhem 1895b, pp. 8-9. The physical and logical relationship between new and old theory, as well as the mathematical difficulty associated to the existence of the function $\mathcal{F}(\alpha, \beta, \dots, \nu, T)$ would have 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 $\alpha, \beta, \dots, \lambda$. Nevertheless, physical and logical objections could be raised against that reduction, although the mathematical generalisation had been apparently accomplished. Duhem was aware that the relationship between his generalized 1891-94 Mechanics/Thermodynamics and his 1895 irreversible Mechanics/Thermodynamics was a very delicate issue. He devoted only a short passage to it, but he acknowledged that the two theories were in some way contradictory. He remarked that they 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 to look upon reversibility as a specific instance of irreversibility.²⁰

There was a very delicate issue even from the mathematical point of view, specifically with regard to the choice of parameters. In fact, the structure of equations (III.5) is not invariant under a general transformation of parameters of the kind

$$\begin{aligned}\alpha &= a(\alpha', \beta', \dots, \nu') \\ \beta &= b(\alpha', \beta', \dots, \nu') \\ &\dots \dots \\ \nu &= n(\alpha', \beta', \dots, \nu')\end{aligned}$$

The replacement of the set of parameters $\alpha, \beta, \dots, \nu$ by the set $\alpha', \beta', \dots, \nu'$, changes the structure of the terms $g_\alpha |d\alpha|, \dots, g_\lambda |d\lambda|$ in (III.5). Only a transformation less general, which does not mix the parameters associated to irreversibility,

²⁰ Duhem 1895b, p. 10.

$$\begin{aligned}
\alpha &= a(\alpha') \\
&\dots\dots \\
\lambda &= l(\lambda') \\
\mu &= m(\mu', \dots, \nu') \\
&\dots\dots \\
\nu &= n(\mu', \dots, \nu')
\end{aligned}$$

could save the invariance of the equations. The mathematical description of the physical system was sensitive to the choice of the parameters: there was, in some way, a sort of mathematical *instability* of the equations.²¹

Nevertheless Duhem went on with other generalisations. The concept of “*natural state*” was generalised into the concept of “*space of natural states*”. It was an abstract space, more specifically a sub-space of the $(2n+1)$ -dimensional space defined by the $(2n+1)$ parameters $\alpha, \beta, \dots, \nu, T$. Natural states corresponded to the conditions $g_\alpha = g_\beta = \dots = g_\lambda = 0$ associated to the equations (III.4):

$$\text{(III.20)} \quad \left\{ \begin{array}{l} g_\alpha(\alpha, \dots, \nu, T, A, B, \dots, N) = 0 \\ \dots\dots \\ g_\lambda(\alpha, \dots, \nu, T, A, B, \dots, N) = 0 \\ M = \frac{\partial \mathcal{F}}{\partial \mu} \\ \dots\dots \\ N = \frac{\partial \mathcal{F}}{\partial \nu} \end{array} \right.$$

There are exactly n equations, and they define a $(n+1)$ -dimensional sub-space of the $(2n+1)$ -dimensional space of the states of the system: it is the space of “*natural states*”.²²

Also the generalization of the concept of closed cycle was based on the equations (III.4-5). Duhem imagined “an infinitely small transformation” after which “the temperature T and the external forces $A, B, \dots, N$ regain their initial values”. If

²¹ Duhem 1895b, pp. 11-2.

²² Duhem 1895b, p. 21.

$\alpha_0, \beta_0, \dots, \nu_0$ are the initial values of the parameters $\alpha, \beta, \dots, \nu$, their final values will generally be different from $\alpha_0, \beta_0, \dots, \nu_0$: he called them $\alpha_1, \beta_1, \dots, \nu_1$. The smallness of the transformation allowed him to perform an approximate integration of the differential equations (III.4-5):

$$\left\{ \begin{array}{l} \frac{\partial^2 \mathcal{F}}{\partial \alpha^2} (\alpha_1 - \alpha_0) + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \alpha} (\nu_1 - \nu_0) + g_\alpha \int |d\alpha| = 0 \\ \dots \dots \\ \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \lambda} (\alpha_1 - \alpha_0) + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \lambda} (\nu_1 - \nu_0) + g_\lambda \int |d\lambda| = 0 \\ \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \mu} (\alpha_1 - \alpha_0) + \dots + \frac{\partial^2 \mathcal{F}}{\partial \nu \partial \mu} (\nu_1 - \nu_0) = 0 \\ \dots \dots \\ \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial \nu} (\alpha_1 - \alpha_0) + \dots + \frac{\partial^2 \mathcal{F}}{\partial^2 \nu} (\nu_1 - \nu_0) = 0 \end{array} \right.$$

The role of the functions $g_\alpha, g_\beta, \dots, g_\lambda$ is quite clear from the mathematical point of view: they prevent the mathematical system of equations to become a homogeneous system. If $g_\alpha = g_\beta = \dots = g_\lambda = 0$, the mathematical system would be homogeneous, and it would offer only the trivial solution $(\alpha_1 - \alpha_0) = \dots = (\nu_1 - \nu_0) = 0$. On the contrary, if some of the functions $g_\alpha, g_\beta, \dots, g_\lambda$ does not vanish, the system is inhomogeneous, and it can offer some non-vanishing solutions for the set of deformations $(\alpha_1 - \alpha_0), \dots, (\nu_1 - \nu_0)$. In the first case, the Lagrangian parameters regain the initial values at the end of the cycle; in the second case they do not. In the first case, the physical system does not experience permanent deformations; in the second case it does.²³

As Duhem himself wrote in the short “Conclusion” at the end of his third paper on permanent deformations, he had shown a possibility: he had outlined a mathematical theory submitted to various specific conditions. Although provisional, the theory

²³ Duhem 1895b, pp. 22-3.

sketched in these papers “cast some light” on a very demanding subject matter.²⁴ Nevertheless, the questions the theory raised were as important as the specific answers it offered. He went on publishing other four papers on the same subject, and under the same title *Sur les déformations permanentes et l’hystérésis*, till 1901. At the same time, he tried to insert the theory of permanent deformations into his *Energetics* or generalised Mechanics. A long essay he published in 1896 represented a further effort of generalisation: it is the subject of the next chapters.

²⁴ 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 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.”

THIRD PART

Towards a general theory of transformations

13. A structural analogy

In 1896, the Parisian librarian and publisher A. Hermann sent to the printing press a long essay Duhem had written for the *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux*. The essay, *Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques*, represented in some way the final stage of Duhem's theoretical, meta-theoretical and historical journey through the complex net of connections involving analytic mechanics, thermodynamics and chemistry. The *structural* analogy based on analytic mechanics, when exploited till its extreme consequences, showed to be deficient in generality. At that stage, Duhem had no other choice that widen the original *structure*, and put forward a wider Mechanics expressed by more general equations. Lagrange's original design of rephrasing mechanics in a more general and abstract way maintained its fruitfulness but, at the end of the nineteenth century, Duhem realized that he had to go a step further.

The *Introduction* to the essay was a theoretical and historical summary intensely focussed on the concept of "false equilibrium" he had introduced three years ago in his *Introduction à la mécanique chimique*. The starting point concerned chemistry, in particular the series of thermo-chemical theories subsequently put forward in the course of that century. Duhem reminded the reader that the more ancient theory 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 takes spontaneously place at low temperatures" but "decompose spontaneously at high temperature". Endothermic combinations should have exhibited the opposite behaviour. The fact was that the law seemed "in opposition with a huge number of specific instances". As in his 1893 book, Duhem chose as example the case of oxygen, hydrogen and water: "gaseous water is produced at the expense of oxygen and hydrogen, and accompanied by a great release of heat". We would expect that, at low temperatures, "most of the gas under consideration be in the state of steam", and, when temperature increases. "the amount of steam in the system decrease". Nevertheless, the expected behaviour had been really observed only at high temperature. On the contrary, at low temperatures, under a given threshold, "a mixture of oxygen, hydrogen and steam can be in equilibrium, irrespective of its composition".

Only under the threshold, at a temperature “close to sombre red”, the mixture underwent combination.¹

In other words, there was a wide region of temperature wherein the equilibrium was maintained by a sort of *laziness* of the system: only over and under that strip the system became sensitive to temperature. Similar “contradictions” were even offered by “endothermic combinations”: silver oxide, for instance, “is produced at the expense of oxygen and silver, and accompanied by an absorption of heat”. At high temperatures, the oxide is produced as expected, but, “at temperatures less than 100°C, silver oxide did not decompose” as expected. The situation which chemists were facing around the middle of the century was thus summarized by Duhem:

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

Cette règle générale peut s’énoncer de la manière suivante :

Toutes les fois que la thermodynamique classique nous annonce l’impossibilité, pour un corps, de subir une certaine modification, la modification dont il s’agit ne peut, en effet, être réalisée expérimentalement ; mais lorsque la thermodynamique classique annonce qu’un corps passera nécessairement d’un état à un autre, il arrive souvent que la modification annoncée ne se réalise pas.”²

Duhem aimed at “developing and completing thermodynamic theories” in order to account for both “true” and “false” equilibrium. What was the more or less hidden “hypothesis” which the exclusion of “false” equilibrium derived from? He thought he had found it in a specific point of his *Commentaires*, just “after having developed the principle of conservation of energy, and before developing Carnot’s principle”. There he had stated that a system defined by its absolute temperature T and its “normal”

¹ Duhem 1896a, pp. 2-4.

² Duhem 1896a, p. 5.

Lagrangian parameters $\alpha, \beta, \dots, \lambda$, is kept in equilibrium by “external actions” $A, B, \dots, L$, which “are specified, **without any ambiguity** in terms of $\alpha, \beta, \dots, \lambda$ and T ”.³ From the mathematical point of view, the flaw was in the system of n equations in $n+1$ parameters

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

When inverted, the system should give the set of values of the parameters $\alpha, \beta, \dots$, and λ corresponding to “a state of equilibrium for the material system, when kept at the temperature T , and submitted to the external forces $A, B, \dots, L$ ”:

$$\begin{cases} \alpha = h_{\alpha}(A, B, \dots, L, T) \\ \beta = h_{\beta}(A, B, \dots, L, T) \\ \dots \dots \\ \lambda = h_{\lambda}(A, B, \dots, L, T) \end{cases} .$$

According to Duhem, even when the last mathematical system gives rise to “an infinity” of solutions, we are not sure that the solutions correspond to “a continuous set of solutions”.⁴

The lack of continuity in the set of solutions was the key concept in Duhem’s comparison between theory and experiments.

³ Duhem 1896a, p. 6. The choice of the bold font for the expression “without any ambiguity” is consistent with the importance Duhem attributed to it.

⁴ Duhem 1896a, pp. 6-7.

“Or, cette supposition est contraire aux propriétés des systèmes qui présentent des états de faux équilibre; 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.*”⁵

The second part of the *Introduction* is devoted to the structural analogy between chemical “false” equilibrium and mechanical “friction”. Duhem took into account a very simple configuration: a body sliding on an inclined plane. According to “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”, it is said that “the body *rubs* against the plane”, and “*classic mechanics does not take into account friction*”. He realized that, in very general terms, the situation could be described by words not so different from the words employed to describe chemical false equilibriums:

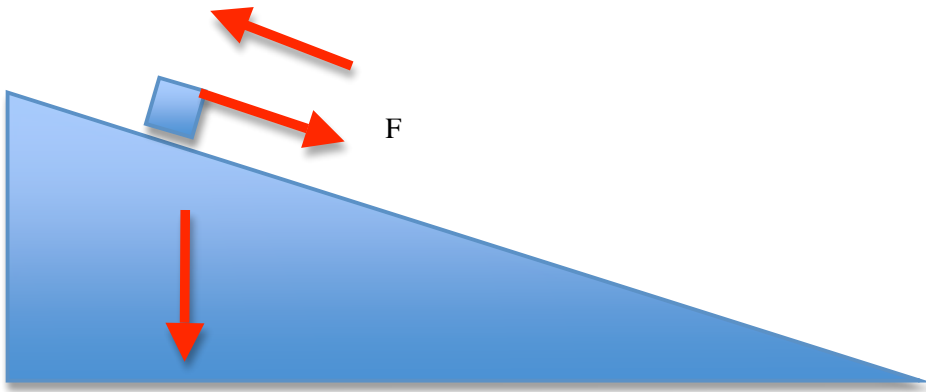
*“Toutes les fois que la mécanique classique classique, où l’on fait abstraction du frottement, fait prévoir qu’un état du système étudié est un état d’équilibre, l’expérience confirme cette conclusion ; mais il peut arriver que le système soit en équilibre dans des états qui ne sont pas des états d’équilibre pour la mécanique des corps sans frottement.”*⁶

The analogy appeared to Duhem not so astonishing as long as “mechanics of bodies without friction is a specific instance of classic thermodynamics”. The existence of a

⁵ Duhem 1896a, p. 7.

⁶ Duhem 1896a, p. 8.

limiting value in the plane inclination α comes easily out from the ordinary procedure of solution of the problem under consideration, 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 but else the opposite of the normal component of P , and a *force* of friction F_a , which is imagined as a force acting upside along the plane. This kind of force is commonly assumed to depend on N and on a coefficient f , which in 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.



P

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

$$f m g \cos \alpha \geq m g \sin \alpha \quad \text{or} \quad \operatorname{tg} \alpha \leq f.^7$$

⁷ Duhem 1896a, p. 9.

Duhem made two remarks: the condition of equilibrium is expressed by an inequality rather than equality, and “the study of friction and the study of false equilibriums show a very close analogy”. More specifically, the two fields of science, although belonging to different fields of science, physics and chemistry, exhibited a formal analogy.

“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.”*⁸

At that point, an important issue emerged from the core of mechanics: is friction a fundamental phenomenon or simply “a *fictitious* term”, roughly describing those “various and complex actions which explain friction” itself? In other words, could “friction” be only a label stuck on a set of “actions whose explicit and detailed analysis is impossible”? Duhem was aware that he was reporting a “widespread opinion”, and he tried to better describe it, in order to better contrast it. According to that opinion, “the equations of mechanics which disregard friction are really general”. Experiments are at variance with the equations only because “natural bodies are more or less rough and pliable”; the disagreement would disappear if only we took into account those “roughness and pliability”. Duhem did not reject completely that “opinion”, since some effects due to friction could be removed by polishing the planes and choosing stiffer bodies. Nevertheless, not all phenomena structurally similar to friction could be reduced to a mere “appearance”, and could be completely described by “classic mechanics”.⁹

He had to overcome both Gibbs’ approach to thermodynamics and his own previous beliefs, for instance the theory of false equilibriums he had outlined in his 1893 *Introduction à la mécanique chimique*. He honestly acknowledged that his “judgement” had changed “on this point”. The “more complex way of representation” he had put

⁸ Duhem 1896a, p. 9.

⁹ Duhem 1896a, pp. 9-11.

forward in 1893 called into play “very energetic actions, even though effective only at small distances”, among “elementary masses”. 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 deficient in generality with regard to 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-exist”. The same theory could explain “*delays in boiling*”, “*delays in condensation*”, “*oversaturation in gaseous solutions*”, and “*delays in decompositions*”.¹⁰

According to Duhem, those phenomena could be classified as “seeming false equilibriums”. They were in accordance with “classic thermodynamic”, provided that we did not confine ourselves to “a too simplified representation of bodies”. Nevertheless, in general, could he be satisfied by that approach? He was aware that he was facing a far-reaching meta-theoretical issue: can we look upon “*laws of mechanics and classic thermodynamics*” as “*logic consequence of unquestioned hypotheses*”? Duhem saw a sharp alternative: to save classic thermodynamics, and apply it to a more sophisticated representation of physical systems, or modify classic mechanics, in order to attain a more general comprehension of complex phenomena. In other words, we can *load* the burden of complexity on the description of physical systems or on the equations of the theory. He was aware that he was dealing with “hypotheses”, or meta-theoretical options, which could not be “disputed”: both of them were rightful meta-theoretical options.

“Si la réponse à cette question est affirmative, une contradiction entre le 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 un plus grande complexité du système abstrait, reproduction schématique des corps sur lesquels on expérimente, auquel on applique ces équations.

¹⁰ Duhem 1896a, pp. 12-13.

Si, au contraire, on répond à cette question par la négative ; si l'on regard 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 compréhensive, 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.”¹¹

The hypothesis on the “conditions of equilibrium” in a physical system could be rejected or accepted. We can rightfully reject the possibility of “determining without any ambiguity” the external actions keeping the system in equilibrium. We are therefore allowed to put into the laws of mechanics and thermodynamics statements which “exclude that possibility”, in order to account for the phenomena of “false equilibrium and friction”. As Duhem remarked, he had already tried to pursue this theoretical pathway in a series of papers published between 1894 and 1895 under the common title *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 followed the *structural* analogy between analytic mechanics on the one hand, and mechanical, thermodynamic and chemical phenomena, on the other. He would have widened the structure of the equations of analytic mechanics, in order to account for those mechanical, thermodynamic and chemical phenomena too complex to be given a suitable description in the framework of classic science.¹²

In the first chapter of the first part of the book, Duhem aimed at resuming “in a more detailed way” the previously sketched “study of viscosity”. He reminded the reader that “the equations of hydrodynamics deduced from D’Alambert principle do not fit the

¹¹ Duhem 1896a, pp. 14-5.

¹² Duhem 1896a, pp. 15-6.

experience”, and that fluids are labelled “*viscous*” just when they do not follow those equations. Then he shortly outlined the history of the interpretations of viscosity in last-century mechanics. He saw essentially two points of view: 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 he had tried to “explain” viscosity as well as “rigidity of elastic solids”. Stokes, on the contrary, had confined himself to introduce “terms corresponding to viscosity in the equations of hydrodynamics”, and had not tried to explain “the origin of these terms”. Duhem found that the distinction between “actual viscosity” and “seeming viscosity” he had put forward in the *Commentaire*, held still true. In other words, there was a kind 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.¹³

Duhem proceeded step by step, following a by now well-known procedure: he started from a simple situation or process and, at every step, put forward further generalisations. He took into account “a system *independent of external bodies*, with the same temperature in every point”, in some way an abstract system. The state of the system was defined by its temperature and a set of “*normal parameters*” $\alpha, \beta, \dots, \lambda$. As usual, in the mathematical-physical toolbox, Duhem put the force vive $\mathfrak{T}$, the internal thermodynamic potential $\mathcal{F}(\alpha, \beta, \dots, \lambda, T)$, and the external forces $A, B, \dots, L$. To those basic functions he added the “*passive resistances*” or “*viscous resistances*” $f_\alpha, f_\beta, \dots, f_\lambda$, depending on the parameters $\alpha, \beta, \dots, \lambda, T$ and the time derivatives $\alpha' = \frac{d\alpha}{dt}, \beta' = \frac{d\beta}{dt}, \dots, \lambda' = \frac{d\lambda}{dt}$. As Duhem remarked, the work done by the “resistances”

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

¹³ Duhem 1896a, pp. 17-9.

“cannot be but negative”.

The generalized Lagrangian equations contained terms of three kinds: purely mechanical, $A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'}$, classic thermodynamical, $\frac{\partial \mathcal{F}}{\partial \alpha}$, and new viscous ones, f_α .

The system was therefore described by the equations

$$(3) \quad \begin{array}{l} A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} - \frac{\partial \mathcal{F}}{\partial \alpha} + f_\alpha = 0 \\ \dots\dots\dots \\ L + \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} - \frac{\partial \mathcal{F}}{\partial \lambda} + f_\lambda = 0 \end{array} \quad .^{14}$$

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

$$(4) \quad dQ = -\left(R_\alpha \cdot d\alpha + R_\beta \cdot d\beta + \dots R_\lambda \cdot d\lambda + C \cdot dT\right)$$

already put forward by Duhem in 1891. The first Principle of thermodynamics, or what Duhem called “the principle of conservation of energy” offered

$$dQ = -dU + \frac{1}{E} d\tau_e \quad \text{or} \quad E dQ = -EdU + d\tau_e.$$

Therefore the differential coefficients $R_\alpha, R_\beta, \dots, R_\lambda, C$ had to obey to the equations

¹⁴ Duhem 1896a, pp. 20-1.

$$\begin{aligned}
 & E \frac{\partial U}{\partial \alpha} - A - \frac{\partial \mathfrak{T}}{\partial \alpha} + \frac{d}{dt} \frac{\partial \mathfrak{T}}{\partial \alpha'} = E R_\alpha \\
 & \dots\dots \\
 (5) \quad & E \frac{\partial U}{\partial \lambda} - L - \frac{\partial \mathfrak{T}}{\partial \lambda} + \frac{d}{dt} \frac{\partial \mathfrak{T}}{\partial \lambda'} = E R_\lambda \cdot \\
 & E \frac{\partial U}{\partial T} = E C
 \end{aligned}$$

The only difference with regard the equations put forward in 1891 was the presence of the living force $\mathfrak{T}$ of the system as a whole.¹⁵

The introduction of the internal potential $\mathcal{F}(\alpha, \beta, \dots, \lambda, T)$ by means of the fundamental relationship

$$EU = \mathcal{F} - T \frac{\partial \mathcal{F}}{\partial T}$$

allowed Duhem to express equations (5) in terms of $\mathcal{F}$:

$$\begin{aligned}
 & \frac{\partial \mathcal{F}}{\partial \alpha} - T \frac{\partial^2 \mathcal{F}}{\partial \alpha \partial T} - A - \frac{\partial \mathfrak{T}}{\partial \alpha} + \frac{d}{dt} \frac{\partial \mathfrak{T}}{\partial \alpha'} = E R_\alpha \\
 & \dots\dots \\
 & \frac{\partial \mathcal{F}}{\partial \lambda} - T \frac{\partial^2 \mathcal{F}}{\partial \lambda \partial T} - L - \frac{\partial \mathfrak{T}}{\partial \lambda} + \frac{d}{dt} \frac{\partial \mathfrak{T}}{\partial \lambda'} = E R_\lambda \cdot \\
 & \frac{\partial \mathcal{F}}{\partial T} - T \frac{\partial^2 \mathcal{F}}{\partial T^2} = E C
 \end{aligned}$$

The most important mathematical and physical step was the transformation of equations (3) into equations for the determination of the functions $f_\alpha, f_\beta, \dots, f_\lambda$:

¹⁵ Duhem 1896a, p. 21. 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, the separation of mechanical and thermal effects: the variation of ϑ did not affect the other parameters, and $\Theta = f_\vartheta = 0$. That choice was combined with the choice $\vartheta = T$.

The presence of irreversibility, corresponding to the presence of the mathematical functions $f_\alpha, f_\beta, \dots, f_\lambda$, made questionable an exact definition of entropy, as Duhem himself had remarked in the papers on permanent deformations. He probably relied on the fact that, in the equations (3) and (6), *reversible* and *irreversible* terms could be mathematically separated. In some way, the burden of irreversibility was loaded on the shoulder of the functions $f_\alpha, f_\beta, \dots, f_\lambda$. This mathematical way out let Duhem to transform equation (4) into the sum of two terms with the help of equations (7):

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

The subsequent step was the integration along a closed cycle of the expression

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

The term containing entropy vanished, and the integral reduced to

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

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

$$\int \frac{dQ}{T} > 0.^{18}$$

¹⁸ Duhem 1896a, p. 23.

The section ended with a sort of recollection and generalisation of the “general theory” he had put forward in 1891. It was in some way a preliminary task, devoted to build up a structure as general as pliable, which could undergo further generalisations.

In the following section Duhem widened the structure tuned in the first section, in order to graft the generalisation put forward in the *Commentaire*: the interaction between the components of a given physical system. He assumed that the system was composed of two parts which Duhem qualified as “independent of each other”, but then 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 $\mathcal{F}_1$ and $\mathcal{F}_2$. The whole system had internal energy and thermodynamic potential which could not simply be the sum of the two functions, because of the unspecified interaction between them. There was a sort of *potential of interaction* Ψ such that, for the whole system,

$$U = Y_1 + Y_2 + \Psi \quad \text{and} \quad \mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2 + E\Psi. ^{19}$$

The “fundamental expression” giving rise to the equations of motion for the two parts considered as “independent systems” was

$$(11) \quad \begin{aligned} & \left(A_1 + \frac{\partial \mathcal{T}_1}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}_1}{\partial \alpha'} - \frac{\partial \mathcal{F}_1}{\partial \alpha} + f_{\alpha_1} \right) \delta \alpha_1 + \\ & + \dots\dots \\ & + \dots\dots \\ & + \left(L_2 + \frac{\partial \mathcal{T}_2}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}_2}{\partial \lambda'} - \frac{\partial \mathcal{F}_2}{\partial \lambda} + f_{\lambda_2} \right) \delta \lambda_2 = 0 \end{aligned}$$

At this point Duhem invited us to “imagine” that some “bilateral” link or contact between the parts 1 and 2 come into play. He was putting forward, in some way, a 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

¹⁹ Duhem 1896a, p. 24.

$$\begin{aligned}
 & M_1 \delta\alpha_1 + \dots + P_1 \delta\lambda_1 + M_2 \delta\alpha_2 + \dots + P_2 \delta\lambda_2 = 0 \\
 (12) \quad & M'_1 \delta\alpha_1 + \dots + P'_1 \delta\lambda_1 + M'_2 \delta\alpha_2 + \dots + P'_2 \delta\lambda_2 = 0 \quad . \\
 & \dots \dots
 \end{aligned}$$

In order to specify the links or bonds acting between the subsets, Duhem introduced the word “welding” (“*soudure*”) for the geometrical-physical action corresponding to the first equation. Duhem did not specify which kind of geometrical or physical action corresponded to the other equations: he confined himself to state that he would have made use of “a similar language for the other bonds.”²⁰

He imagined a hierarchy of bonds which were activated one after the other when the two subsets approached to each other. Every bond, when activated, triggered a new kind of “viscous resistance”, and a new term appeared in the equations of motion. There was a hierarchy of “viscosities”

$$\begin{aligned}
 & f_{\alpha_1} + F_{\alpha_1} + F'_{\alpha_1} + \dots \\
 & \dots \dots \\
 & f_{\lambda_1} + F_{\lambda_1} + F'_{\lambda_1} + \dots \\
 & f_{\alpha_2} + F_{\alpha_2} + F'_{\alpha_2} + \dots' \\
 & \dots \dots \\
 & f_{\lambda_2} + F_{\lambda_2} + F'_{\lambda_2} + \dots
 \end{aligned}$$

which corresponded to a series of waste of energy expressed by the inequalities

$$\begin{aligned}
 & \left(f_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + f_{\lambda_1} \frac{d\lambda_1}{dt} \right) dt \leq 0 \\
 & \left(f_{\alpha_2} \frac{d\alpha_2}{dt} + \dots + f_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt \leq 0 \quad , \\
 & \left(F_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + F_{\lambda_1} \frac{d\lambda_1}{dt} + F_{\alpha_2} \frac{d\alpha_2}{dt} + \dots + F_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt \leq 0 \\
 & \left(F'_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + F'_{\lambda_1} \frac{d\lambda_1}{dt} + F'_{\alpha_2} \frac{d\alpha_2}{dt} + \dots + F'_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt \leq 0 \quad .
 \end{aligned}$$

²⁰ Duhem 1896a, pp. 25-6. Duhem made use of the word “*soudure*” besides “*liaison*” and “*contact*”.

$$\frac{d^2\alpha_1}{dt^2}, \dots, \frac{d^2\lambda_1}{dt^2}, \frac{d^2\alpha_2}{dt^2}, \dots, \frac{d^2\lambda_2}{dt^2}$$

were the (n_1+n_2) terms $\frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'}$. The set of equations (16) could therefore be considered as a system of (n_1+n_2) equations with regard to the (n_1+n_2+p) unknown quantities

$$(17) \frac{d^2\alpha_1}{dt^2}, \dots, \frac{d^2\lambda_1}{dt^2}, \frac{d^2\alpha_2}{dt^2}, \dots, \frac{d^2\lambda_2}{dt^2}, \Pi, \Pi', \dots$$

What about the missing p equations? They were offered by the double time-derivative of the set of p equations (12): as Duhem remarked, they become “ p linear equations in

$$\frac{d^2\alpha_1}{dt^2}, \dots, \frac{d^2\lambda_1}{dt^2}, \frac{d^2\alpha_2}{dt^2}, \dots, \frac{d^2\lambda_2}{dt^2},”^{22}$$

According to Duhem, the mathematical problem associated to a “viscous” physical system had a solution, since it consisted of “a system of (n_1+n_2+p) linear equations in the (n_1+n_2+p) unknown quantities (17)”. The solution would have allowed us to determine those quantities as functions of the parameters $\alpha_1, \beta_1, \dots, \lambda_1, T_1, \alpha_2, \beta_2, \dots, \lambda_2, T_2$ and their time-derivatives $\frac{d\alpha_1}{dt}, \frac{d\beta_1}{dt}, \dots, \frac{d\lambda_1}{dt}, \frac{d\alpha_2}{dt}, \frac{d\beta_2}{dt}, \dots, \frac{d\lambda_2}{dt}$. This was the output of the complex mathematical machinery, which required an as much complex input. Duhem reminded the reader that we should know “the analytic expression” of $A_1, \dots, L_2, M_1, \dots, P_2, M'_1, \dots, P'_2, \mathcal{T}, \mathcal{F}, f_{\alpha_1}, \dots, f_{\lambda_1}, f_{\alpha_2}, \dots, f_{\lambda_2}, F_{\alpha_1}, \dots, F_{\lambda_1}, F_{\alpha_2}, \dots, F_{\lambda_2}$, and $F'_{\alpha_1}, \dots, F'_{\lambda_1}, F'_{\alpha_2}, \dots, F'_{\lambda_2}$.²³

The specific thermodynamic account followed the pathway already outlined in the previous section: at first the total heat expressed in terms of mechanical and thermal *coefficients*,

²² Duhem 1896a, pp. 30-1.

²³ Duhem 1896a, pp. 31-2.

$$dQ = -\left(R_{\alpha_1} \cdot d\alpha_1 + R_{\beta_1} \cdot d\beta_1 + \dots R_{\lambda_1} \cdot d\lambda_1 + C_1 \cdot dT_1\right) \\ -\left(R_{\alpha_2} \cdot d\alpha_2 + R_{\beta_2} \cdot d\beta_2 + \dots R_{\lambda_2} \cdot d\lambda_2 + C_2 \cdot dT_2\right),$$

and then the expressions for every coefficient:

$$E \frac{\partial U}{\partial \alpha_1} - A_1 - \frac{\partial \mathcal{T}}{\partial \alpha_1} + \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'_1} = E R_{\alpha_1}.$$

.....

At the end, the total heat was expressed in terms of entropy and “viscous forces”:

$$dQ = -T_1 dS_1 - T_2 dS_2 \\ - \frac{1}{E} \left(f_{\alpha_1} \frac{d\alpha_1}{dt} + f_{\beta_1} \frac{d\beta_1}{dt} + \dots + f_{\lambda_1} \frac{d\lambda_1}{dt} \right) dt, \\ - \frac{1}{E} \left(f_{\alpha_2} \frac{d\alpha_2}{dt} + f_{\beta_2} \frac{d\beta_2}{dt} + \dots + f_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt \\ dQ = - \frac{1}{E} \left(F_{\alpha_1} \frac{d\alpha_1}{dt} + F_{\beta_1} \frac{d\beta_1}{dt} + \dots + F_{\lambda_1} \frac{d\lambda_1}{dt} + F_{\alpha_2} \frac{d\alpha_2}{dt} + F_{\beta_2} \frac{d\beta_2}{dt} + \dots + F_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt \\ - \frac{1}{E} \left(F'_{\alpha_1} \frac{d\alpha_1}{dt} + F'_{\beta_1} \frac{d\beta_1}{dt} + \dots + F'_{\lambda_1} \frac{d\lambda_1}{dt} + F'_{\alpha_2} \frac{d\alpha_2}{dt} + F'_{\beta_2} \frac{d\beta_2}{dt} + \dots + F'_{\lambda_2} \frac{d\lambda_2}{dt} \right) dt.$$

Because of the negative sign of the “work done by viscous forces”,

$$dQ \geq -T_1 dS_1 - T_2 dS_2,$$

in accordance with the second Principle of Thermodynamics. The result could be generalised to a system composed of q rather than 2 parts:

$$dQ \geq -T_1 dS_1 - T_2 dS_2 - \dots - T_q dS_q.$$

$$T_1 dS_1 + T_2 dS_2 + \dots + T_q dS_q \geq 0,$$

In the next section, Duhem put forward a further generalisation: a system which was not isolated from “external bodies”. In order to reduce the new configuration to the previous one, Duhem made the system under consideration correspond to the subsystem labelled “1”, and “external bodies” to “bodies considered as such in the previous section, and added to body 2”. In the “equations of motion” of the system, there was nothing different from the previous case:

$$A_1 + \frac{\partial \mathcal{T}_1}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}_1}{\partial \alpha'} - \frac{\partial \mathcal{F}_1}{\partial \alpha} + f_{\alpha_1} + F_{\alpha_1} + F'_{\alpha_1} + \dots + \Pi M_1 + \Pi' M'_1 + \dots = 0$$

²⁴ Duhem 1896a, pp. 33-6. In the texts there are some misprints in equations and inequalities involving dQ .

$$\begin{aligned}
 E \frac{dQ}{T_1} = & -E dS_1 - \frac{1}{T_1} \left(f_\alpha \frac{d\alpha}{dt} + f_\beta \frac{d\beta}{dt} + \dots + f_\lambda \frac{d\lambda}{dt} \right) dt \\
 (37) \quad & - \frac{1}{T_1} \left(F_\alpha \frac{d\alpha}{dt} + F_\beta \frac{d\beta}{dt} + \dots + F_\lambda \frac{d\lambda}{dt} \right) dt,^{25} \\
 & - \frac{1}{T_1} \left(F'_\alpha \frac{d\alpha}{dt} + F'_\beta \frac{d\beta}{dt} + \dots + F'_\lambda \frac{d\lambda}{dt} \right) dt
 \end{aligned}$$

“viscous” works had not the same fundamental features. Apart from the term

$$f_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + f_{\lambda_1} \frac{d\lambda_1}{dt},$$

which corresponded to the “intrinsic viscosity” of the system, and having therefore a negative sign, the other “works” had an unpredictable sign. As Duhem remarked, we have “no information” about the sign of the expressions

$$F_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + F_{\lambda_1} \frac{d\lambda_1}{dt} + F'_{\alpha_1} \frac{d\alpha_1}{dt} + \dots + F'_{\lambda_1} \frac{d\lambda_1}{dt}.$$

He did not further inquire into this important issue: why cannot we foresee the sign? The fact is that, differently from an isolated system, wherein the fluxes of energy are submitted to definite conditions, a body in interaction with external bodies could give and receive energy in many different ways.

“Ainsi, lorsqu’on un système de température uniforme présente avec les corps extérieures des liaisons bilatérales, il n’est plus juste de dire, en général, que la transformation compensée $(-E dS_1/dt)dt$ 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 :

²⁵ Duhem 1896a, p. 44. In this page there are some misprints, Duhem’s plus/minus dysgraphie included.

Lorsqu'on un système, de température à chaque instant uniforme, qui présente avec les corps extérieurs des liaisons 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 ; ...”²⁶

²⁶ Duhem 1896a, pp. 44-5.

14. Further generalisations and astonishing differences

As Duhem remarked, he had already introduced the mathematical terms corresponding to viscosity in the third part of his *Commentaire*. The first Part of his 1896 essay was essentially a formal development or “the natural consequence” of the assumptions there introduced. On the contrary, the second Part of the present essay tried to go “beyond a fundamental hypothesis” which the theory had been based on, namely the unambiguous determination of the equilibrium. Before putting forward the new generalisation, Duhem introduced a purely mathematical transformation on the Lagrangian parameters $\alpha, \beta, \dots, \lambda$: at the moment, it was a very general linear transformation, devoid of any physical meaning. The non-singular transformation and its reverse were represented by the two linear systems

$$(82) \quad \begin{aligned} \delta a &= \mu_{11} \delta \alpha + \mu_{12} \delta \beta + \dots + \mu_{1n} \delta \lambda \\ \delta b &= \mu_{21} \delta \alpha + \mu_{22} \delta \beta + \dots + \mu_{2n} \delta \lambda \\ &\dots \dots \\ \delta l &= \mu_{n1} \delta \alpha + \mu_{n2} \delta \beta + \dots + \mu_{nn} \delta \lambda \end{aligned} \quad \text{and} \quad (82') \quad \begin{aligned} \delta \alpha &= \mu'_{11} \delta a + \mu'_{12} \delta b + \dots + \mu'_{1n} \delta l \\ \delta \beta &= \mu'_{21} \delta a + \mu'_{22} \delta b + \dots + \mu'_{2n} \delta l \\ &\dots \dots \\ \delta \lambda &= \mu'_{n1} \delta a + \mu'_{n2} \delta b + \dots + \mu'_{nn} \delta l \end{aligned}$$

The forces $A, B, \dots, L$, the gradient of the potential $\mathcal{F}$, viscous forces, and the Lagrangian terms involving $\mathcal{T}$ were transformed as well according to the following typographic choice:

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

The equations of motion were then formally expressed by the equations

¹ Duhem 1896a, pp. 67-8 and 70.

$$\left\{ \begin{array}{l} \mathcal{A} - \Phi_a + J_a + \varphi_a = 0 \\ \mathcal{B} - \Phi_b + J_b + \varphi_b = 0 \\ \dots\dots \\ \mathcal{L} - \Phi_l + J_l + \varphi_l = 0 \end{array} \right. .^2$$

From a very general point of view, every equation consisted 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 new “FUNDAMENTAL HYPOTHESIS”, corresponding to the introduction of a new term in the equations of motion:

$$(93) \quad \left\{ \begin{array}{l} \mathcal{A} - \Phi_a + J_a + \varphi_a + g_a \frac{a'}{|a'|} = 0 \\ \mathcal{B} - \Phi_b + J_b + \varphi_b + g_b \frac{b'}{|b'|} = 0 \\ \dots\dots \\ \mathcal{L} - \Phi_l + J_l + \varphi_l + g_l \frac{l'}{|l'|} = 0 \end{array} \right. .$$

The new functions $g_a, g_b, \dots, g_l$ were negative functions, and depended on the Lagrangian parameters $a, b, \dots, l$, their time-derivatives $a', b', \dots, l'$, and the forces $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$. Differently from the “viscous” forces $f_a, f_b, \dots, f_\lambda$ (or $\varphi_a, \varphi_b, \dots, \varphi_\lambda$), they could not vanish when the velocities $a', b', \dots, l'$ vanished: on the contrary, they tended to the limiting functions $\gamma_a, \gamma_b, \dots, \gamma_\lambda$, which depended only on $a, b, \dots, l$ and $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$. The terms of the kind $g_a \cdot a'/|a'|$ generalised the static friction of Mechanics discussed in the *Introduction*. This explains why they could not vanish with the generalised velocities. As expected, the “work done by friction”,

² Duhem 1896a, pp. 70-2.

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

was negative.³

At this point, Duhem also explained the physical meaning of the linear mathematical transformation on the Lagrangian parameters $\alpha, \beta, \dots, \lambda$. He was looking for a transformation which could split the mathematical representation of the physical system into two complementary sub-representations: the parameters corresponding to the mechanical “motion” of the system as a whole, on the one hand, and the parameters corresponding to the other generalised “motions”, on the other.

*“Parmi les n quantités infiniment petites $\delta a, \delta b, \dots, \delta l$, données par les égalités (82), il en est six $\delta m, \dots, \delta n$ qui jouissent de la propriété suivante : lorsque celles-là seules diffèrent de zéro, le système éprouve un déplacement d’ensemble dans l’espace, sans que ses diverses parties éprouvent ni changement d’état, ni changement de position relative ; celles des quantités $g_a, g_b, \dots, g_l$ qui leur correspondent sont identiquement nulles.”*⁴

As a consequence of the choice of the parameters $a, b, \dots, l$, which should have allowed Duhem to split the physical phenomenon into two qualitatively different processes, two different sets of conditions of equilibrium emerged. The first set corresponded to the parameters and the external actions suffering friction; the second set corresponded to the six parameters describing the purely mechanical motion “of the system as a whole”. The latter was nothing else but the condition of equilibrium for a “invariable solid body”.

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

³ Duhem 1896a, pp. 72-5.

⁴ Duhem 1896a, p. 74.

$$(98) \begin{cases} \gamma_a \leq \mathcal{A} - \Phi_a \leq -\gamma_a \\ \gamma_b \leq \mathcal{B} - \Phi_b \leq -\gamma_b \\ \dots\dots \\ \gamma_l \leq \mathcal{L} - \Phi_l \leq -\gamma_l \end{cases} \quad \text{and} \quad (95) \begin{cases} \mathcal{M} - \Phi_m = 0 \\ \dots\dots\dots \\ \mathcal{N} - \Phi_n = 0 \end{cases} .''^5$$

The first set of inequalities described the “*infinities of states of equilibrium, which classic thermodynamics was not able to foresee*”. It is not strange that they were expressed by inequalities when we make still reference to the structural analogy with static friction put forward in the *Introduction*.

The remaining part of the chapter offered no surprise: the “total transformation” dQ/T was the sum of the “compensated” term $-dS$ and the “uncompensated” term corresponding to “viscosity” and “friction”:

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

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

La transformation non compensée qui accompagne une modification réelle ne peut jamais être négative ; en général elle est positive.”⁶

The last section of the chapter was devoted to systems “composed of independent parts with different temperatures”. Apart from the presence of the potential of interaction Ψ , submitted to the same linear transformation operating on the Lagrangian parameters, the equations of motion had the same structure:

⁵ Duhem 1896a, p. 77.

⁶ Duhem 1896a, pp. 83-4.

$$\left\{ \begin{array}{l} \mathcal{A}_1 - E\Psi_{a_1} - \Phi_{a_1} + J_{a_1} + \varphi_{a_1} + g_{a_1} \frac{a'_1}{|a'_1|} = 0 \\ \mathcal{B}_1 - E\Psi_{b_1} - \Phi_{b_1} + J_{b_1} + \varphi_{b_1} + g_{b_1} \frac{b'_1}{|b'_1|} = 0 \\ \dots\dots \\ \mathcal{L}_1 - E\Psi_{l_1} - \Phi_{l_1} + J_{l_1} + \varphi_{l_1} + g_{l_1} \frac{l'_1}{|l'_1|} = 0 \end{array} \right. .$$

A similar set of equations had to be written for the part 2 of the system, and the same mathematical procedure led to “Clausius’ inequality extended to the system under consideration”.⁷

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

In the second chapter of the second Part, he tried a specific application, and, at the same time, tried to bridge the gulf between physics and chemistry. The “specific systems”, which he devoted his attention to, were those “usually studied in the context of chemical mechanics”. He imagined a system composed of two parts of “masses” M_1 and M_2 ; then he defined a set of “normal” parameters $T, \alpha, \beta, \dots, \lambda$, 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 $\alpha, \beta, \dots, \lambda$. The only external action acting on the whole 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 :

$$V = V_1 + V_2 = M_1 v_1 + M_2 v_2 .$$

The external work $d\mathcal{T}$ performed by the external force P was

⁷ Duhem 1896a, pp. 84-8.

$$\begin{aligned}
d\mathcal{T} &= -P dV = -PM_1 dv_1 - PM_2 dv_2 - Pv_1 dM_1 - Pv_2 dM_2 = \\
&= -PM_1 dv_1 - PM_2 dv_2 \\
&\quad - Pv_1 \left(\frac{\partial M_1}{\partial \alpha} d\alpha + \dots + \frac{\partial M_1}{\partial \lambda} d\lambda \right) \\
&\quad - Pv_2 \left(\frac{\partial M_2}{\partial \alpha} d\alpha + \dots + \frac{\partial M_2}{\partial \lambda} d\lambda \right)
\end{aligned}$$

If we assemble the terms corresponding to every parameter, the expression for the work reduced to

$$\begin{aligned}
d\mathcal{T} &= -PM_1 dv_1 - PM_2 dv_2 \\
&\quad - P \left(v_1 \frac{\partial M_1}{\partial \alpha} d\alpha + v_2 \frac{\partial M_2}{\partial \alpha} d\alpha \right) \\
&\quad - \dots \\
&\quad - P \left(v_1 \frac{\partial M_1}{\partial \lambda} d\lambda + v_2 \frac{\partial M_2}{\partial \lambda} d\lambda \right)
\end{aligned}$$

The only “external force”, the ordinary pressure P , gave therefore rise to a series of “external actions” $\Pi_1, \Pi_2, A, B, \dots, L$, corresponding to the parameters v_1, v_2 and $\alpha, \beta, \dots, \lambda$:

$$\begin{aligned}
\Pi_1 &= -PM_1 \\
\Pi_2 &= -PM_2 \\
(137) \quad A &= -P \left(v_1 \frac{\partial M_1}{\partial \alpha} + v_2 \frac{\partial M_2}{\partial \alpha} \right)^8 \\
&\quad \dots \\
L &= -P \left(v_1 \frac{\partial M_1}{\partial \lambda} + v_2 \frac{\partial M_2}{\partial \lambda} \right)
\end{aligned}$$

After having applied the mathematical transformations (82) to the parameters $\alpha, \beta, \dots, \lambda$, Duhem assumed that “viscosity and friction” corresponding to the parameters v_1, v_2 could be neglected, and the “inertial force” could be neglected too. He

⁸ Duhem 1896a, pp. 89-90.

expressed the equation of motion for the parameters v_1, v_2 in accordance with the old mathematical representation:

$$\begin{aligned} PM_1 + \frac{\partial \mathcal{F}}{\partial v_1} &= 0 \\ PM_2 + \frac{\partial \mathcal{F}}{\partial v_2} &= 0 \end{aligned} .$$

On the contrary, the equations corresponding to $\alpha, \beta, \dots, \lambda$ were expressed in the transformed representation:

$$(139) \left\{ \begin{array}{l} \mathcal{A} - \Phi_a + \varphi_a + g_a \frac{a'}{|a'|} = 0 \\ \mathcal{B} - \Phi_b + \varphi_b + g_b \frac{b'}{|b'|} = 0 \\ \dots \dots \\ \mathcal{L} - \Phi_l + \varphi_l + g_l \frac{l'}{|l'|} = 0 \end{array} \right. .$$

At this point Duhem called into play the thermodynamic potential $H = \mathcal{F} + PV$, a suitable potential for physical-chemical processes taking place at constant pressure. He showed that

$$\begin{aligned} \frac{\partial H}{\partial \alpha} &= \frac{\partial \mathcal{F}}{\partial \alpha} + \frac{\partial(PV)}{\partial \alpha} = \frac{\partial \mathcal{F}}{\partial \alpha} + P \frac{\partial(M_1 v_1 + M_2 v_2)}{\partial \alpha} = \\ &= \frac{\partial \mathcal{F}}{\partial \alpha} + P \left(v_1 \frac{\partial M_1}{\partial \alpha} d\alpha + v_2 \frac{\partial M_2}{\partial \alpha} d\alpha \right) \end{aligned} ,$$

⁹ Duhem 1896a, pp. 90-1. 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 fact 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 essay.

since the parameters v_1, v_2 are independent of α . From the equations (137) we have that

$$(147) \quad \frac{\partial H}{\partial \alpha} = \frac{\partial \mathcal{F}}{\partial \alpha} - A$$

After having submitted $\partial H / \partial \alpha$ and the other derivatives to the linear transformation (82),

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

equation (147) became

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

and the equations of motion (139) assumed the more simplified structure

$$(150) \quad \left\{ \begin{array}{l} \eta_a - \varphi_a - g_a \frac{a'}{|a'|} = 0 \\ \dots\dots\dots \\ \eta_l - \varphi_l - g_l \frac{l'}{|l'|} = 0 \end{array} \right. .^{10}$$

These equations seemed to Duhem “very convenient” with regard 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 making recourse to specific mechanical models. On the

¹⁰ Duhem 1896a, pp. 92-3. Duhem’s potential H corresponded to Massieu’s potential H and Gibb’s potential Φ .

other hand, the equations above displayed could offer an invariant structure, “independent of” the choice of the parameters and the specific expressions for $\varphi_\alpha, \varphi_\beta, \dots, \varphi_\lambda$ and $g_a, g_b, \dots, g_l$. In the last section of the chapter, Duhem outlined a similar mathematical procedure for a set of Lagrangia parameters $\alpha, \beta, \dots, \lambda, T, V$, instead of $\alpha, \beta, \dots, \lambda, T, P$.¹¹

For the subsequent analysis of some chemical processes, it was important to take note of some inequalities involving $\partial H / \partial \alpha, \dots, \partial H / \partial \lambda$. From the set of equations (150),

$$\left\{ \begin{array}{l} \eta_a = \varphi_a + g_a \frac{a'}{|a'|} \\ \dots\dots \\ \eta_l = \varphi_l - g_l \frac{l'}{|l'|} \end{array} \right. \quad \text{and} \quad \left\{ \begin{array}{l} \eta_a \frac{da}{dt} = \varphi_a \frac{da}{dt} + g_a \frac{a'}{|a'|} \frac{da}{dt} \\ \dots\dots \\ \eta_l \frac{dl}{dt} = \varphi_l \frac{dl}{dt} - g_l \frac{l'}{|l'|} \frac{dl}{dt} \end{array} \right. .$$

The sum of all these equations led to the single equation

$$\eta_a \frac{da}{dt} + \dots\dots + \eta_l \frac{dl}{dt} = \varphi_a \frac{da}{dt} + \dots\dots + \varphi_l \frac{dl}{dt} + g_a \frac{a'}{|a'|} \frac{da}{dt} + \dots\dots + g_l \frac{l'}{|l'|} \frac{dl}{dt} .$$

Since the dissipative terms perform a negative work, the right side of the last equation is negative:

$$\eta_a \frac{da}{dt} + \dots\dots + \eta_l \frac{dl}{dt} < 0 .$$

When expressed in terms of $\partial H / \partial \alpha, \dots, \partial H / \partial \lambda$ and the old parameters $\alpha, \beta, \dots, \lambda$, the inequality can be written as

¹¹ Duhem 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.

$$(154) \quad \frac{\partial H}{\partial \alpha} \frac{d\alpha}{dt} + \dots + \frac{\partial H}{\partial \lambda} \frac{d\lambda}{dt} < 0.^{12}$$

In the third chapter, Duhem claimed he was dealing with “systems already studied in the previous chapter”, but he rather resumed the graphical methods put forward in the papers on permanent deformations and hysteresis. From the outset 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 in part of non-transformed functions and in part of transformed ones, Duhem wrote the equation of motion once again:

$$(169) \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \varphi(P, \alpha, T, \alpha') - g(P, \alpha, T, \alpha') \frac{\alpha'}{|\alpha'|} = 0.$$

When friction corresponding to the parameter α vanished, the equation was reduced to

$$(168) \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} = 0.^{13}$$

It represents a curve in the plane (T, α) : Duhem reminded the reader that it is “the curve of true equilibrium” under the constant pressure P . In general, friction does exist, and tends towards the negative function $\gamma(P, \alpha, T)$ when α tends to zero. The condition of equilibrium for the system under consideration was a “specific instance” of the inequalities (98):

$$(170) \quad \gamma(P, \alpha, T) \leq \frac{\partial H(P, \alpha, T)}{\partial \alpha} \leq -\gamma(P, \alpha, T).$$

¹² Duhem 1896a, pp. 94-5.

¹³ Duhem 1896a, pp. 99-100.

Duhem pointed out that the two curves in the plane (T, α) corresponding to the equations

$$(170') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) = 0 \quad \text{and} \quad (170'') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) = 0$$

were as important as the curve of “true equilibrium”. They represent the boundaries of the “region of false equilibrium”, wherein the conditions (170) are satisfied.¹⁴

The curves of true equilibrium can be ascending or descending curves, according to the endothermic or exothermic behaviour of the physical system. Starting from a state of true equilibrium under constant pressure and temperature, represented by a point on the curve, let us increase the parameter α . If the system undergoes an absorption of heat ($R_\alpha > 0$), then the new point of equilibrium will be found on the right and above the previous one: the curve of true equilibrium “will rise from left to right”. The opposite behaviour will be expected when the transformation will lead to an emission of heat ($R_\alpha < 0$).

The curve represented by equation (170') will be always found above the curve of true equilibrium, because the function $\gamma(P, \alpha, T)$ is always negative. For the same reason, the curve corresponding to equation (170'') will be always found below the curve of true equilibrium. To sum up, “the curve of true equilibrium is completely plotted inside the region of false equilibrium”. Outside that region, the system is out of equilibrium: it will undergo a transformation.¹⁵

Because of equation (170'), on the corresponding curve,

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

For the same reason, on the other curve,

¹⁴ Duhem 1896a, pp. 100-1.

¹⁵ Duhem 1896a, pp. 100-1.

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

Duhem also remarked that, below the curve corresponding to (170''), $\frac{\partial H(P, \alpha, T)}{\partial \alpha} < 0$, and a series of deductions led him to state that $\alpha' = \frac{d\alpha}{dt} > 0$. In a simpler way, we can notice that, from equation (154), when the system is only described by a parameter α ,

$$\frac{\partial H}{\partial \alpha} \frac{d\alpha}{dt} < 0.$$

If, below the curve corresponding to (170''), $\frac{\partial H(P, \alpha, T)}{\partial \alpha} < 0$, then $\alpha' > 0$; if, above the curve corresponding to (170'), $\frac{\partial H(P, \alpha, T)}{\partial \alpha} > 0$, then $\alpha' < 0$.¹⁶

Similar “considerations” could be applied to transformations taking place at constant volume, and described by the potential $F(V, \alpha, T)$. The condition of equilibrium would correspond to the inequalities

$$\Gamma(V, \alpha, T) \leq \frac{\partial F(V, \alpha, T)}{\partial \alpha} \leq -\Gamma(V, \alpha, T),$$

and the condition of true equilibrium to the equation

$$\frac{\partial F(V, \alpha, T)}{\partial \alpha} = 0.¹⁷$$

¹⁶ Duhem 1896a, p. 101.

¹⁷ Duhem 1896a, pp. 101-2.

At this stage, some phenomenological remarks came into play, and Duhem gave them the form of 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 with temperature.

“HYPOTHESE - Lorsque la variation de la variable α constitue un changement d'état chimique, les deux fonctions positives

$$\begin{aligned} &-\gamma(P, \alpha, T), \\ &-\Gamma(V, \alpha, T) \end{aligned}$$

décroissent sans cesse lorsque la température croît ; elles ont des 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.”¹⁸

The region of false equilibrium was wide at low temperatures, and became narrower when temperature increased; for high temperatures, the region was reduced to nothing else but 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 temperature that “states of equilibrium extremely different from those expected on the basis of classic thermodynamics” really occurred. Classic thermodynamics did not take into account the generalisation of the concept of “friction”: therefore it could only account for real phenomena at high temperature. For this reason, as Duhem remarked, “*chemical mechanics gives place to simpler laws at high rather low temperatures*”.

The concept of “friction” in Duhem’s generalized physics stemmed from a structural analogy between Mechanics and Chemistry. The word “friction” made sense in the

¹⁸ Duhem 1896a, p. 104.

context of Chemistry only after a re-interpretation of the ordinary meaning. The behaviour of thermo-chemical processes with regard to temperature transformed the formal analogy into a more realistic analogy: the increase of temperature played in Chemistry the same role of the increase of smoothness in Mechanics. High temperature dissolved *chemical* friction as well a better smoothness dissolved mechanical friction. Duhem remarked that modern Mechanics was born when Galileo decided to neglect mechanical friction. He had given birth to a very simplified physics: Duhem was accomplishing the demanding task of realising a more complete and realistic physics.

“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.”¹⁹

In this third chapter of the second part of his essay, Duhem faced for the first time a specific chemical problem, with the help of phenomenological (T, α) diagrams. He took into account a chemical “compound together with the elements coming from its decomposition”. Then he labelled the mass of the compound m , and “the greater mass of the compound consistent with the constitution of the system” M . The Lagrangian parameter

$$\alpha = \frac{m}{M}$$

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

¹⁹ Duhem 1896a, p. 105.

complete as possible”. Duhem assumed, in particular, that the chemical process were exothermic ($R_\alpha < 0$) and took place at constant volume.

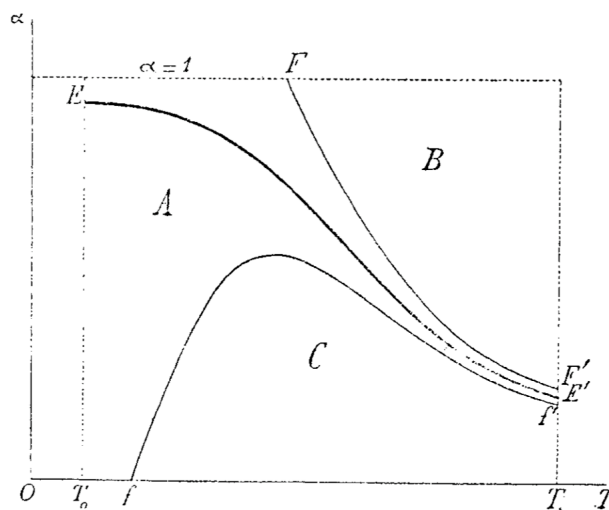


FIG. 1.

20

In Duhem's graph, EE' is the curve of “true equilibrium”, and FF' and ff'' are curves describing the boundaries of the region A of “false equilibrium”. The region B “is the seat of a dissociation”, and the region C is “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.

“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

²⁰ From Duhem 1896a, p. 106.

combinaison. C'est seulement à températures élevées que les deux limites sont sensiblement égales entre elles."²¹

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

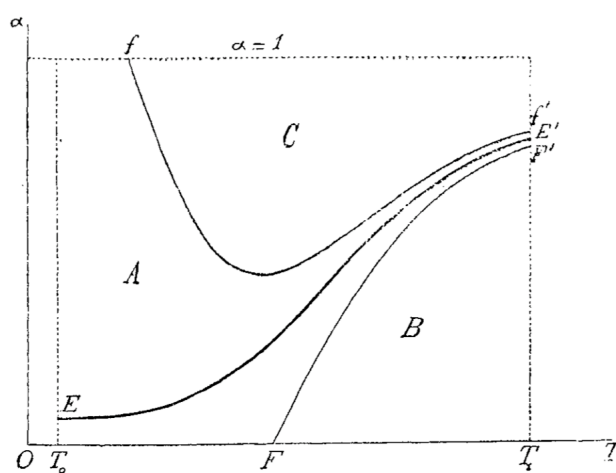


FIG. 2.

22

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 suggested by Duhem in the first pages of this essay is clear: a body cannot slide along an inclined plane until the horizontal component of the gravitational force overwhelm the static friction between the body and the plane. In the chemical side of the analogy, a chemical compound is placed in presence of its components: the mixture is in equilibrium until the chemical *forces* become so strong to trigger a chemical reaction of combination or decomposition.

²¹ Duhem 1896a, pp. 106-7.

²² From Duhem 1896a, p. 107.

Following the geometrical representation of this kind of processes, 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 axe OT ”. The system will remain in the region of false equilibrium for a while, until its representative line will cross 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.”²³

The concept of false equilibrium was tightly close 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 the system”, both at constant volume and pressure. Among the infinite point 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 observation of the point of combination. When heated either at constant volume

²³ Duhem 1896a, p. 109.

or pressure, the two gases “remain blended” in a state of false equilibrium until a certain temperature is reached: after that the combination begins.²⁴

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. Others chemical reactions were very active at ordinary temperatures, since their point of reaction was placed at very low temperatures. Instances of the latter, shortly discussed by Duhem, were “the mixture of frozen sulphuric acid and caustic soda, or the mixture of “sulphuric acid and potassium”.²⁵

The remaining part of the chapter was devoted to a detailed analysis of different kinds of chemical reactions in physical systems wherein “the different points have different temperatures”.

In the fourth chapter, the formal analogy between Mechanics and Chemistry underwent a critical stress. Duhem focused his attention in particular on the concept of “velocity”, and the chapter headline was indeed “Velocity of reactions”. He reminded the reader that, in the “*region of combination*”, placed below the curve ff' , $\alpha' > 0$; in the “*region of decomposition*”, above the curve FF' , $\alpha' < 0$. In both regions, the transformations, or chemical “reactions” had to obey to the generalised equation of *motion* (169):

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

Nevertheless, in the region of combination, $|\alpha'| = +\alpha'$, and therefore the equation of *motion* becomes

$$(176) \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \varphi(P, \alpha, T, \alpha') - g(P, \alpha, T, \alpha') = 0.$$

²⁴ Duhem 1896a, pp. 109-10.

²⁵ Duhem 1896a, pp. 110-11.

On the contrary, in the region of decomposition, $|\alpha| = -\alpha'$, and the equation of *motion* becomes

$$(176') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \varphi(P, \alpha, T, \alpha') + g(P, \alpha, T, \alpha') = 0. \text{ }^{26}$$

From these equations, Duhem 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 then that

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

being the limiting function $\gamma(P, \alpha, T)$ independent of α' . Then he assumed that the function $\varphi(P, \alpha, T, \alpha')$, expressing the “viscosity” of the system, depended on α' in a very simple way:

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

Even though the first simplification was quite sharp, both of them appeared to Duhem “the simplest”, and “definitely verified” for small values of $|\alpha|$. According to these simplifications, equations (176) and (176') became

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) - \Phi(P, \alpha, T) \alpha' = 0,$$

²⁶ Duhem 1896a, pp. 127-8.

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) - \Phi(P, \alpha, T) \alpha' = 0. \quad {}^{27}$$

The simplified equations allowed him to give a simple expression for the “velocity” of reaction in chemical processes, because α' appears only in the factorisation of the third term:

$$(179) \quad \alpha' = \frac{\frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T)}{\Phi(P, \alpha, T)},$$

$$(179') \quad \alpha' = \frac{\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T)}{\Phi(P, \alpha, T)}.$$

Duhem’s simplified theory entailed a predictable behaviour of “velocity”. It 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

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

The denominator decreased when “viscosity” decreased, namely when the system approached classic thermodynamic behaviour.²⁸

The structural analogy between Mechanics and Thermo-Chemistry required that increasing *smoothness* in the first field corresponded to 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 $\Phi(P, \alpha, T)$ decreased with temperature.

²⁷ Duhem 1896a, p. 128.

²⁸ Duhem 1896a, pp. 129 and 131. There is a plus/minus misprint in the equation (170^{ter}).

“L’expérience nous apprend que la valeur absolue de la vitesse d’une réaction donnée croît 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.”*²⁹

The two dissipative effects Duhem had introduced in the equations of *motion*, namely “viscosity” and “friction”, had the same behaviour with regard temperature: the intensity of temperature freed the system from dissipative effects. Although Duhem’s generalised physics, which included mechanics, thermodynamics and chemistry, was based on the *structural* analogy between physics and chemistry, he acknowledged the “essential differences” between “the theory of motion of systems as taught by Dynamics” and his “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 the differential equation involving acceleration. In Duhem’s theory of false equilibrium, velocity was the outcome of a mathematical procedure starting from the knowledge of 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 $\frac{d^2\alpha}{dt^2}$ 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 $\frac{d\alpha}{dt}$* , 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

²⁹ Duhem 1896a, p. 131. Duhem’s previous hypothesis concerning the thermo-chemical behaviour of a system with regard temperature can be found at page 104.

de transformation $\frac{d\alpha}{dt}$ 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 des semblables modifications.*"³⁰

The last sentence of Duhem's passage refers probably to the mathematical and conceptual partnership between "inertia" and acceleration in Newton's second law. He had looked upon his generalised physics as a generalisation of classic dynamics, involving systems undergoing dissipation, but now he realised that he had arrived at a sharp mathematical and conceptual gap between mechanics and chemistry. In the outcome of his theory of chemical false equilibrium he saw a contrast rather than a generalisation. He realised that, starting from a *structural* analogy, he had reached a *structural* difference between classic dynamics and his generalised physics.

In the mathematical model of false equilibrium, two issues were at stake. First, the role played by acceleration in ordinary mechanics was played by velocity in chemistry. Second, when the generalised viscosity vanished, velocity became infinite: this limiting case did not correspond to modern mechanics but to Aristotle mechanics. In order to better explain the theoretical break, Duhem compared a pendulum undergoing free oscillations with a damped pendulum. Starting from free oscillations, we could imagine gradually increasing viscosity acting on the pendulum, until it becomes critically damped, and it approaches asymptotically the position of equilibrium without any oscillation. Velocity assumes oscillating finite values decreasing with the increasing viscosity, until it vanishes asymptotically. In the ordinary mechanical framework, whatever case of infinite velocity is excluded. On the contrary, in Duhem framework, the starting point was represented by a system strongly damped: 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 reduced to each other. In particular, processes like swinging pendulum cannot be looked upon as specific instances of Duhem generalised processes.

If we try to reverse Duhem process, starting from "motions" free from viscosity, we have an infinite velocity. When we increase viscosity, the velocity diminishes, but

³⁰ Duhem 1896a, p. 130.

cannot vanish unless the system is found on the boundaries of the region of false equilibrium. This is what we can deduce by Duhem mathematical model, at least in the simplified version expressed by equations (179) and (179'). 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: the equations cannot account for the limiting case of motion without dissipation. In other words, the equations do not represent a generalisation of classic Dynamics: motion without viscosity would make sense only if the numerator vanished as well, namely only “when the representative point describes one of the curves FF' or ff'' ”.³¹

When Duhem emphasised the “essential differences” between his general theory and classic Dynamics, he had in mind the above outlined creaks at the borderline between mathematical *structure* and physical phenomena. In some way, 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 velocity be determined by the knowledge of forces. Moreover it is not strange that, in absence of some kind of resistance by an all-pervading medium, velocity becomes infinite.

However, those difficulties did not prevent Duhem from inquiring into chemical reactions with the help of his theory.

³¹ Duhem 1896a, pp. 130-1.

15. From explosions down to mechanical friction

In the last two chapters of his 1896 essay, 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 of chemical systems. Duhem remarked that the region of false equilibrium, wherein $\frac{d\alpha}{dt}=0$, was a region of “*indifferent*” equilibrium. The region of combination, placed below the curve ff' (in the case of exothermic reactions), was a seat of stability, since $d\alpha/dt > 0$: the point representative of the system moves upside, towards the region of false equilibria. The region of dissociation, placed above the curve FF' , was a seat of stability as well. In fact, $d\alpha/dt < 0$, and the point representative of the system must move downside. Duhem then wondered whether a state corresponding to the “*limiting state of false equilibrium*”, defined by the equations

$$(170') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) = 0 \quad \text{or} \quad (170'') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) = 0,$$

were a “stable” or “indifferent” state. 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”.¹

First of all Duhem demonstrate the stability of isothermal transformations which start from a state represented by a point $M_0(\alpha_0, T_0)$ on the curve ff' : the co-ordinates of the starting point satisfy equation (170''). According to Duhem, the final point $M_1(\alpha_1, T_1)$ could be found in three different places: inside the region of false equilibrium, still on the curve ff' , or in the region of combination. For the first and the second case, he wrote

$$\frac{\partial H(P, \alpha_1, T_1)}{\partial \alpha_1} + \gamma(P, \alpha_1, T_1) > 0 \quad \text{and} \quad \frac{\partial H(P, \alpha_1, T_1)}{\partial \alpha_1} + \gamma(P, \alpha_1, T_1) = 0$$

¹ Duhem 1896a, pp. 139-40 and 142.

respectively. In both cases, the “disturbance” of the system did not move it away from equilibrium: in summary, “the equilibrium of the system is indifferent”. In the third case, the point $M_1(\alpha_1, T_1)$ is in the region of combination, wherein $d\alpha/dt > 0$. This means that the value of the parameter α must increase, leading the representative point upside, towards its starting point, the curve ff' of the limiting states of false equilibrium. In summary, “the equilibrium is stable”. Not so different remarks would lead to the stability of a transformation starting from a state represented by a point on the curve FF' .²

In the case of adiabatic transformations, “the law of variation of temperature” was required. Both the first Principle of Thermodynamics and Duhem’s expression for dQ in terms of its thermal coefficients lead to

$$dQ = -(R_\alpha d\alpha - C dT).$$

In adiabatic transformations, $dQ = 0$, and therefore

$$(185) \quad R_\alpha d\alpha = C dT \quad \text{or} \quad \frac{dT}{dt} = -\frac{R_\alpha}{C} \frac{d\alpha}{dt} = -\frac{R_\alpha}{C} \alpha'.$$

Duhem assumed that the representative point M_0 was on the curve FF' , wherein

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

² Duhem 1896a, p. 141. Duhem’s choice of symbols is quite unfortunate. In an isothermal transformation, the representative point of the system must move along a vertical line in the plane (T, α) : therefore we have $M_0(\alpha_0, T_0)$ and $M_1(\alpha_1, T_1)$. Moreover the derivative $\partial H(P, \alpha_1, T_1)/\partial \alpha_1$ should be written as $[\partial H(P, \alpha, T)/\partial \alpha]_{\alpha=\alpha_1}$.

and that the subsequent point M_1 was not inside the region of false equilibrium, wherein the system did not undergo further transformations, and the stability was assured. He therefore assumed that M_1 was in the region of dissociation, wherein

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) > 0 \quad \text{and} \quad \frac{d\alpha}{dt} < 0.$$

In the region of false equilibrium, there was a transition from the condition

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

corresponding to the line FF' , to the condition

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

corresponding to the central line of “true” equilibrium. The condition corresponding to such a region was therefore

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) < 0.$$

As a consequence, Duhem assumed that the stability of the system was assured by the condition

$$\frac{d}{dt} \left[\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) \right] < 0,$$

namely the condition that, starting from the state represented by M_1 , the expression

$$\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T)$$

could only decrease. Under this condition, every adiabatic transformation will be “impossible”, and the system will keep its stability. After having developed the derivation, the condition of stability becomes

$$\frac{d}{d\alpha} \left[\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) \right] \frac{d\alpha}{dt} + \frac{d}{dT} \left[\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) \right] \frac{dT}{dt} < 0.^3$$

Equation (185) helps us to remove the time-derivative of temperature:

$$\frac{d}{d\alpha} \left[\frac{\partial H}{\partial \alpha} + \gamma \right] \frac{d\alpha}{dt} + \frac{d}{dT} \left[\frac{\partial H}{\partial \alpha} + \gamma \right] \left(-\frac{R_\alpha}{C} \frac{d\alpha}{dt} \right) < 0,$$

$$\left[\frac{\partial^2 H}{\partial \alpha^2} + \frac{\partial \gamma}{\partial \alpha} \right] \frac{d\alpha}{dt} - \frac{R_\alpha}{C} \left[\frac{\partial^2 H}{\partial \alpha \partial T} + \frac{\partial \gamma}{\partial T} \right] \frac{d\alpha}{dt} < 0,$$

$$\left[C \left(\frac{\partial^2 H}{\partial \alpha^2} + \frac{\partial \gamma}{\partial \alpha} \right) - R_\alpha \left(\frac{\partial^2 H}{\partial \alpha \partial T} + \frac{\partial \gamma}{\partial T} \right) \right] \frac{d\alpha}{dt} < 0.$$

Being M_1 in the region where $d\alpha/dt < 0$, the condition of stability becomes

$$(186) \quad C \left(\frac{\partial^2 H}{\partial \alpha^2} + \frac{\partial \gamma}{\partial \alpha} \right) - R_\alpha \left(\frac{\partial^2 H}{\partial \alpha \partial T} + \frac{\partial \gamma}{\partial T} \right) > 0.$$

Duhem summarised the results in the following way:

“Ainsi, un état de faux équilibre limite en lequel l'égalité

³ Duhem 1896a, pp. 142-3.

$$(170') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T) = 0$$

est vérifiée sera un équilibre stable si le système est maintenu dans une enveloppe imperméable à la chaleur et si en cet état l'égalité [sic] (186) est vérifiée.

On démontrerait de même qu'un état de faux équilibre en lequel l'égalité

$$(170'') \quad \frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) = 0$$

est vérifiée sera un équilibre stable si le système est maintenu dans une enveloppe imperméable à la chaleur et si en cet état l'inégalité

$$(186') \quad C \left(\frac{\partial^2 H}{\partial \alpha^2} - \frac{\partial \gamma}{\partial \alpha} \right) - R_\alpha \left(\frac{\partial^2 H}{\partial \alpha \partial T} - \frac{\partial \gamma}{\partial T} \right) > 0.$$

est vérifiée.”⁴

Duhem found that inequalities (186) and (186'), which expressed mathematically the stability of a system under adiabatic transformations, were also involved in the study of “explosive reactions”. Nevertheless, in this case 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. In this different approach, the starting point was represented by the simplified equations for the “velocity of reaction” Duhem had discussed in the previous chapter. Those equations represented a very critical stage in the building up of his generalised physics, but had shown to be useful in the context of Chemistry. The two equations

$$(179) \quad \alpha' = \frac{\frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T)}{\Phi(P, \alpha, T)} \quad \text{and} \quad (179') \quad \alpha' = \frac{\frac{\partial H(P, \alpha, T)}{\partial \alpha} + \gamma(P, \alpha, T)}{\Phi(P, \alpha, T)},$$

corresponded to “combination” and “dissociation” regions, wherein $d\alpha/dt > 0$ and $d\alpha/dt < 0$ respectively. The two equations can be synthesised in the single equation

⁴ Duhem 1896a, p. 144.

$$(179'') \frac{d\alpha}{dt} = \frac{\frac{\partial H(P, \alpha, T)}{\partial \alpha} - \gamma(P, \alpha, T) \frac{\alpha'}{|\alpha'|}}{\Phi(P, \alpha, T)},$$

which became the starting point for the computation of the acceleration. After the time-derivation, Duhem found

$$(187) \frac{d^2\alpha}{dt^2} = \frac{1}{\Phi} \left[\left(\frac{\partial^2 H}{\partial \alpha^2} - \frac{\partial \gamma}{\partial \alpha} \frac{\alpha'}{|\alpha'|} \right) \frac{d\alpha}{dt} + \left(\frac{\partial^2 H}{\partial \alpha \partial T} - \frac{\partial \gamma}{\partial T} \frac{\alpha'}{|\alpha'|} \right) \frac{dT}{dt} \right] - \frac{\frac{\partial H}{\partial \alpha} - \gamma \frac{\alpha'}{|\alpha'|}}{\Phi^2} \left(\frac{\partial \Phi}{\partial \alpha} \frac{d\alpha}{dt} - \frac{\partial \Phi}{\partial T} \frac{dT}{dt} \right).$$

Under the hypothesis that the representative point of the state of the system was “infinitely close to the two curves ff' or FF' , which enclosed the region of false equilibrium”, the term $\frac{\partial H}{\partial \alpha} - \gamma \frac{\alpha'}{|\alpha'|}$ could be considered “infinitely small”. Therefore equation (187) came down to

$$(188) \frac{d^2\alpha}{dt^2} = \frac{1}{\Phi} \left[\left(\frac{\partial^2 H}{\partial \alpha^2} - \frac{\partial \gamma}{\partial \alpha} \frac{\alpha'}{|\alpha'|} \right) \frac{d\alpha}{dt} + \left(\frac{\partial^2 H}{\partial \alpha \partial T} - \frac{\partial \gamma}{\partial T} \frac{\alpha'}{|\alpha'|} \right) \frac{dT}{dt} \right].^5$$

As already shown, equation (185) helps us to remove the time-derivative of temperature:

$$(191) \frac{d^2\alpha}{dt^2} = \frac{1}{C\Phi} \left[C \left(\frac{\partial^2 H}{\partial \alpha^2} - \frac{\partial \gamma}{\partial \alpha} \frac{\alpha'}{|\alpha'|} \right) - R_\alpha \left(\frac{\partial^2 H}{\partial \alpha \partial T} - \frac{\partial \gamma}{\partial T} \frac{\alpha'}{|\alpha'|} \right) \right] \frac{d\alpha}{dt}.$$

In the “*region of combination*”, $d\alpha/dt > 0$ and $\Phi < 0$: $\frac{d^2\alpha}{dt^2}$ has the same sign of the expression

⁵ Duhem 1896a, pp. 151-2.

$$-\left[C\left(\frac{\partial^2 H}{\partial \alpha^2}-\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}-\frac{\partial \gamma}{\partial T}\right)\right].$$

Therefore $\frac{d^2 \alpha}{dt^2} > 0$ when $C\left(\frac{\partial^2 H}{\partial \alpha^2}-\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}-\frac{\partial \gamma}{\partial T}\right) < 0$, and $\frac{d^2 \alpha}{dt^2} < 0$ when $C\left(\frac{\partial^2 H}{\partial \alpha^2}-\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}-\frac{\partial \gamma}{\partial T}\right) > 0$. In the first case, the positive “velocity” of the chemical reaction increases, and becomes “explosive”; in the second case the reaction slows down. This is consistent with the condition of stability (186’) already discussed by Duhem in the first section of the chapter.

In the “*region of dissociation*”, $d\alpha/dt < 0$ and $\Phi < 0$: $\frac{d^2 \alpha}{dt^2}$ has the same sign of the expression

$$\left[C\left(\frac{\partial^2 H}{\partial \alpha^2}+\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}+\frac{\partial \gamma}{\partial T}\right)\right].$$

Therefore $\frac{d^2 \alpha}{dt^2} > 0$ when $C\left(\frac{\partial^2 H}{\partial \alpha^2}+\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}+\frac{\partial \gamma}{\partial T}\right) > 0$, and $\frac{d^2 \alpha}{dt^2} < 0$ when $C\left(\frac{\partial^2 H}{\partial \alpha^2}+\frac{\partial \gamma}{\partial \alpha}\right)-R_{\alpha}\left(\frac{\partial^2 H}{\partial \alpha \partial T}+\frac{\partial \gamma}{\partial T}\right) < 0$. In the first case, the negative “velocity” of the chemical reaction changes positively, and the reaction becomes milder; in the second case it becomes explosive. Once again, this is consistent with Duhem’s condition of stability (186).⁶

⁶ Duhem 1896a, p. 154. There is a misprint in Duhem equation (191): the term C is missing immediately after the squared brackets. The conditions for explosive or mild reactions in the case of dissociations, when compared to the case of combinations, could appear somehow puzzling. It could be useful a graphic interpretation, wherein “acceleration of reaction” is nothing else but the concavity of a function. For increasing functions, a positive second derivative means a sharper increase; for decreasing functions, a positive second derivative means a milder decrease.

“Un système, enfermé dans une enveloppe imperméable à la chaleur, est dans un état voisin d’un faux équilibre limite ; la valeur absolue de la vitesse de la modification dont le système est le siège est une fonction croissante ou décroissante du temps, selon que le faux équilibre limite au voisinage duquel se trouve le système est instable ou stable dans les conditions considérées.

Convenons désormais de nommer *explosion* une réaction dont la vitesse croît en valeur absolue avec le temps lorsque le système est maintenu dans une enveloppe imperméable à la chaleur ; *réaction modérée*, une réaction dont la vitesse, dans les mêmes conditions, décroît en valeur absolue lorsque le temps croît ; nous pourrions énoncer comme suit le théorème précédent :

*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.”*⁷

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.

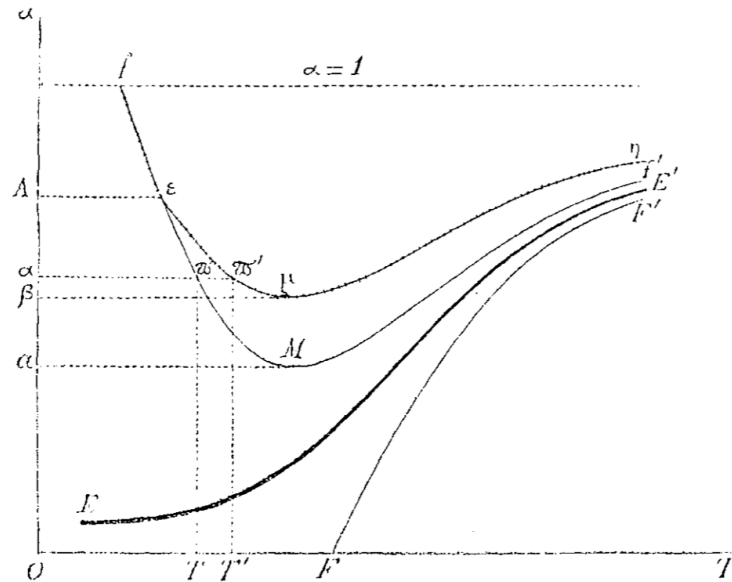
⁷ Duhem 1896a, p. 155.

Au dessus de cette ligne $\eta\eta'$ (fig. 15), on a $\frac{d^2\alpha}{dt^2} < 0$ et la combinaison est modérée ; au-dessous de cette ligne, on a $\frac{d^2\alpha}{dt^2} > 0$ et la combinaison est explosive.”⁸

The line $\eta\eta'$ corresponded to the condition

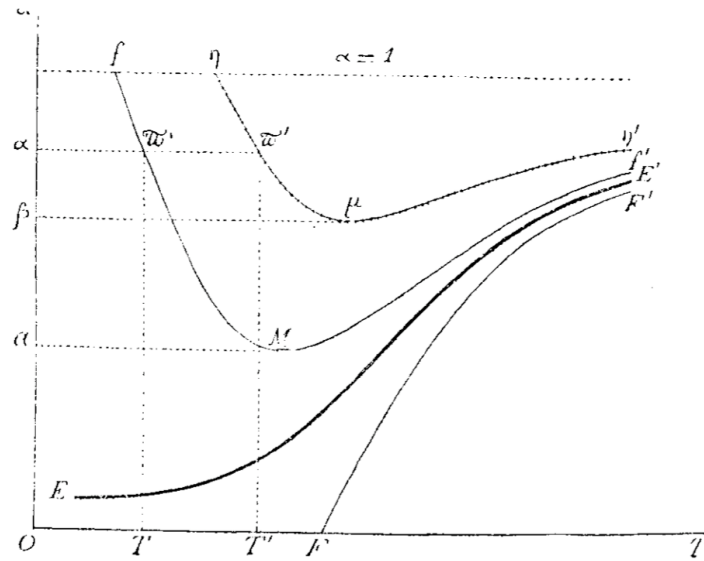
$$C \left(\frac{\partial^2 H}{\partial \alpha^2} - \frac{\partial \gamma}{\partial \alpha} \right) - R_\alpha \left(\frac{\partial^2 H}{\partial \alpha \partial T} - \frac{\partial \gamma}{\partial T} \right) = 0.$$

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.



Picture 3 (Duhem 1896a, p. 162)

⁸ Duhem 1896a, p. 163.



Picture 4 (Duhem 1896a, p. 166)

“... il peut arriver que, dans cette région de décomposition, il existe un ligne $\eta\eta'$ (fig. 16) définie par l'égalité $\frac{d^2\alpha}{dt^2}=0$; au-dessous d'une telle ligne, on a $\frac{d^2\alpha}{dt^2}>0$ et la décomposition du système, au sein d'une enveloppe imperméable à la chaleur, est une décomposition modérée; au-dessous d'une telle ligne, on a $\frac{d^2\alpha}{dt^2}<0$ et la décomposition du système est explosive.”⁹

Duhem was aware that the 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; that the living force does not undergo “negligible variations”. In sudden and violent phenomena like explosions, those simplifications were definitely unsuitable. 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.

⁹ Duhem 1896a, p. 165.

“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.”¹⁰

With the help of three new hypotheses, Duhem rephrased the study of combinations, in particular the propagation of “WAVES OF COMBINATION”. Nevertheless, at the end, he found that even the new theoretical inquiry was based on “hypotheses which could not be realised”: for instance, neither viscosity nor “diffusion” could be neglected in real chemical reactions, which are not purely adiabatic. Taming complexity was found too hard to be pursued in a completely satisfactory way. The general equations of the kind (93) had shown to be potentially fruitful in order to describe a wide set of phenomena, but the theory creaked 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 tried to insist on specific applications. He discussed the structure of his general equations but, at the end, he invited the reader to make reference to a brief bibliography for assumptions.

“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 :”¹¹

He rather tried to widen the scope of his general equations describing two interacting bodies, by removing a previous “restriction” on the bonds between the bodies: in fact, surfaces of separation had been assumed “welded together”. He described the first body

¹⁰ Duhem 1896a, p. 168.

¹¹ Duhem 1896a, p. 178.

by means of a set of n_1 parameters, apart from its temperature T_1 : some of them, $a_1, \dots, l_1$, described the internal state of the system, and suffered friction, while at least six of them, $m_1, \dots, n_1$, described the system as a whole, and were free from friction. The second body was described by a similar set of n_2 parameters, and by its temperature T_2 .

“Les modifications virtuelles principales ... pour lesquelles il n’y a pas de frottement, peuvent être plus ou moins nombreuses ; mais leur nombre ne peut être inférieure à 6 ; parmi elles, en effet, se trouvent forcément six modifications qui déterminent un changement de position absolue dans l’espace du système formé par l’ensemble des corps 1 and 2, sans changement d’état et sans changement de situation relative de ses diverses parties.”¹²

The internal energy and therefore the internal thermodynamic potential depended on a term of interaction Ψ , which was independent of the temperature T_1 and T_2 :

$$U = U_1 + U_2 + \Psi \quad \text{and} \quad \mathcal{F} = \mathcal{F}_1 + \mathcal{F}_2 + E \Psi.$$

The “virtual work” done by “external actions” applied to systems 1 and 2 were respectively

$$\begin{aligned} &(\mathcal{A}_1 + \mathcal{A}'_1)\delta a_1 + \dots (\mathcal{L}_1 + \mathcal{L}'_1)\delta l_1 + \dots (\mathcal{N}_1 + \mathcal{N}'_1)\delta n_1 \\ &(\mathcal{A}_2 + \mathcal{A}'_2)\delta a_2 + \dots (\mathcal{L}_2 + \mathcal{L}'_2)\delta l_2 + \dots (\mathcal{N}_2 + \mathcal{N}'_2)\delta n_2. \end{aligned}$$

Notwithstanding the complexity of the physical system, and the interaction between the two bodies, Duhem assumed that the system was separable in two senses. In the first sense, the generalised *motion* of the system could be split into a change of *state* and a change of *position*, corresponding to two separate sub-sets of parameters. In the second

¹² Duhem 1896a, p. 188.

sense, the virtual work could be split into the work done by truly external actions, and the work done by forces of interactions between the two parts of the system. If the first contribution was

$$\mathcal{A}_1 \delta a_1 + \dots + \mathcal{L}_1 \delta l_1 + \dots + \mathcal{N}_1 \delta n_1 + \mathcal{A}_2 \delta a_2 + \dots + \mathcal{L}_2 \delta l_2 + \dots + \mathcal{N}_2 \delta n_2,$$

the second corresponded to the potential of interaction Ψ :

$$\mathcal{A}'_1 \delta a_1 + \dots + \mathcal{L}'_1 \delta l_1 + \dots + \mathcal{N}'_1 \delta n_1 + \mathcal{A}'_2 \delta a_2 + \dots + \mathcal{L}'_2 \delta l_2 + \dots + \mathcal{N}'_2 \delta n_2.^{13}$$

The theory Duhem had put forward in the first and third chapter of the essay entailed three sets of equations: two equations of *motion* of the kind equation (93), and an equation for the *bonds*, of the kind equation (12). In symbols,

$$(213) \left\{ \begin{array}{l} \mathcal{A}_1 + \mathcal{A}'_1 - {}^1\Phi_{a_1} + J_{a_1} + \varphi_{a_1} + g_{a_1} \frac{a_1'}{|a'_1|} = 0 \\ \dots \dots \\ \mathcal{L}_1 + \mathcal{L}'_1 - {}^1\Phi_{l_1} + J_{l_1} + \varphi_{l_1} + g_{l_1} \frac{l_1'}{|l'_1|} = 0 \\ \mathcal{M}_1 + \mathcal{M}'_1 - {}^1\Phi_{m_1} + J_{m_1} + \varphi_{m_1} = 0 \\ \dots \dots \\ \mathcal{N}_1 + \mathcal{N}'_1 - {}^1\Phi_{n_1} + J_{n_1} + \varphi_{n_1} = 0 \end{array} \right. ,$$

$$(213') \left\{ \begin{array}{l} \mathcal{A}_2 + \mathcal{A}'_2 - {}^2\Phi_{a_2} + J_{a_2} + \varphi_{a_2} + g_{a_2} \frac{a_2'}{|a'_2|} = 0 \\ \dots \dots \\ \mathcal{L}_2 + \mathcal{L}'_2 - {}^2\Phi_{l_2} + J_{l_2} + \varphi_{l_2} + g_{l_2} \frac{l_2'}{|l'_2|} = 0 \\ \mathcal{M}_2 + \mathcal{M}'_2 - {}^2\Phi_{m_2} + J_{m_2} + \varphi_{m_2} = 0 \\ \dots \dots \\ \mathcal{N}_2 + \mathcal{N}'_2 - {}^2\Phi_{n_2} + J_{n_2} + \varphi_{n_2} = 0 \end{array} \right. ,$$

¹³ Duhem 1896a, pp. 184-5. Duhem choice of symbols was unfortunate and quite puzzling. I have tried to simplify the notation, in order to make it consistent with the remaining part of the essay.

and

$$\begin{aligned}
 & \alpha_1 \delta \alpha_1 + \dots + \Gamma_1 \delta \lambda_1 + \alpha_2 \delta \alpha_2 + \dots + \Gamma_2 \delta \lambda_2 + p \delta p + \dots + q \delta q + r \delta r + \dots + s \delta s = 0 \\
 (215) \quad & \alpha'_1 \delta \alpha_1 + \dots + \Gamma'_1 \delta \lambda_1 + \alpha'_2 \delta \alpha_2 + \dots + \Gamma'_2 \delta \lambda_2 + p' \delta p + \dots + q' \delta q + r' \delta r + \dots + s' \delta s = 0 . \\
 & \dots \dots
 \end{aligned}$$

Duhem specified that the terms ${}^1\Phi_{a_1}$, ..., in equation (213) depended only on the potential $\mathcal{F}_1$, as well as ${}^2\Phi_{a_2}$, ..., depended only on the potential $\mathcal{F}_2$. The equations corresponding to parameters of the kind $m_1, \dots, n_1$ did not contain the term of “friction”. In equations (215), the new parameters $p, \dots, q$, and $r, \dots, s$ were introduced by Duhem in a pure mathematical way as “*linear and homogeneous functions*” of $m_1, \dots, n_1$ and $m_2, \dots, n_2$.¹⁴

The physical meaning of the new parameters emerged when he tried to write equations of *motion* of the greatest generality. Instead of two sets of equations, one for the parameters of the kind $a_1, \dots, l_1$, and the other for the parameters of the kind $m_1, \dots, n_1$, he wrote three kinds of equations: one for $a_1, \dots, l_1, a_2, \dots, l_2$, one for $p, \dots, q$, and one for $r, \dots, s$. Moreover, he introduced the new functions

$$\begin{aligned}
 \Phi_{a_1} &= {}^1\Phi_{a_1} - \mathcal{A}'_1, \quad \Phi_{a_2} = {}^2\Phi_{a_2} - \mathcal{A}'_2, \quad \dots \dots, \\
 G_{a_1}, \dots, G_{l_1}, G_{a_2}, \dots, G_{l_2}, G_p, \dots, G_q.
 \end{aligned}$$

The functions $G_{a_1}, \dots, G_{l_1}, G_{a_2}, \dots, G_{l_2}$ could be identified with the old functions $g_{a_1}, \dots, g_{l_1}, g_{a_2}, \dots, g_{l_2}$. The new functions $G_p, \dots, G_q$ depended on the generalised forces $\mathcal{A}_1, \dots, \mathcal{L}_1, \mathcal{A}_2, \dots, \mathcal{L}_2, \mathcal{P}, \dots, \mathcal{Q}, \mathcal{R}, \dots, \mathcal{S}$ only through the coefficients $\Pi, \Pi', \dots$ of the linear combination of equations (215). The general equations had the following structure:

¹⁴ Duhem 1896a, pp. 185-7.

$$\begin{cases}
\mathcal{A}_1 + \Pi \alpha_1 + \Pi' \alpha'_1 + \dots - \Phi_{a_1} + J_{a_1} + \varphi_{a_1} + G_{a_1} \frac{a_1'}{|a'_1|} = 0 \\
\dots\dots\dots \\
\mathcal{L}_1 + \Pi \mathfrak{l}_1 + \Pi' \mathfrak{l}'_1 + \dots - \Phi_{l_1} + J_{l_1} + \varphi_{l_1} + G_{l_1} \frac{l_1'}{|l'_1|} = 0 \\
\dots\dots\dots \\
\mathcal{A}_2 + \Pi \alpha_2 + \Pi' \alpha'_2 + \dots - \Phi_{a_2} + J_{a_2} + \varphi_{a_2} + G_{a_2} \frac{a_2'}{|a'_2|} = 0 \\
\dots\dots\dots \\
\mathcal{L}_2 + \Pi \mathfrak{l}_2 + \Pi' \mathfrak{l}'_2 + \dots - \Phi_{l_2} + J_{l_2} + \varphi_{l_2} + G_{l_2} \frac{l_2'}{|l'_2|} = 0
\end{cases}$$

$$\begin{cases}
\mathcal{P} + \Pi \mathfrak{p} + \Pi' \mathfrak{p}' + \dots - \Phi_p + J_p + \varphi_p + G_p \frac{p'}{|p'|} = 0 \\
\dots\dots\dots \\
\mathcal{Q} + \Pi \mathfrak{q} + \Pi' \mathfrak{q}' + \dots - \Phi_q + J_q + \varphi_q + G_q \frac{q'}{|q'|} = 0
\end{cases}$$

$$\begin{cases}
\mathcal{R} + \Pi \mathfrak{r} + \Pi' \mathfrak{r}' + \dots - \Phi_r + J_r + \varphi_r = 0 \\
\dots\dots\dots \\
\mathcal{S} + \Pi \mathfrak{s} + \Pi' \mathfrak{s}' + \dots - \Phi_s + J_s + \varphi_s = 0
\end{cases}^{15}$$

The first set of equations for $a_1, \dots, l_1, a_2, \dots, l_2$ corresponded to transformations undergoing some kind of intrinsic friction. The second set of equations for $p, \dots, q$ corresponded to transformations wherein only the bonds gave place to some kind of friction. The third set of equations for $r, \dots, s$ corresponded to transformations free from friction.

The great effort of generalisation led to the usual generalisation of the concept of heat as the sum of all effects of all kinds of transformations. Once again, Duhem final step was the proof of the inequality

$$(238) \quad dS + \sum \frac{dQ}{T} > 0$$

for whatsoever transformation, and to “Clausius’ inequality” for closed cycles:

¹⁵ Duhem 1896a, pp. 187, 189-90.

$$(239) \int \sum \frac{dQ}{T} > 0.^{16}$$

The summary Duhem outlined in his “Conclusion” was, in some way, a plan for further researches. The first passages were just devoted to “Clausius’ inequalities”: generalised viscosity and friction, because of the corresponding negative work, led naturally to inequalities (238) and (239). 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 had a satisfactory explanation in the negative work performed by dissipative actions and permanent deformations. At this point Duhem asked the fundamental question: what is the specific feature “the term of *viscosity*, the term of *friction*, and the term of *hysteresis*” have in common, and differentiate them from the other “terms already contained” in the equations? According to Duhem, the specific feature is the behaviour with regard time, in particular time-symmetry.

Under the transformation $t \rightarrow -t$, the first time-derivatives $\frac{d\alpha}{dt}, \dots, \frac{d\lambda}{dt}$ transform into $-\frac{d\alpha}{dt}, \dots, -\frac{d\lambda}{dt}$, whereas the second time-derivatives $\frac{d^2\alpha}{dt^2}, \dots, \frac{d^2\lambda}{dt^2}$ remains invariant.

Purely mechanical equations of the kind

$$\begin{aligned} A + \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} - \frac{\partial \mathcal{F}}{\partial \alpha} &= 0 \\ \dots\dots\dots \\ L + \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} - \frac{\partial \mathcal{F}}{\partial \lambda} &= 0 \end{aligned}$$

contain only quadratic terms in $\frac{d\alpha}{dt}, \dots, \frac{d\lambda}{dt}$, and therefore they are invariant under the transformation $t \rightarrow -t$, even though $\frac{d\alpha}{dt}, \dots, \frac{d\lambda}{dt}$ are not. In summary, equations of ordinary Mechanics are invariant under time-symmetry.

¹⁶ Duhem 1896a, p. 196.

“Il résulte de là que si un système peut éprouver une modification déterminée, ..., il peut également, sous l’influence des mêmes actions, parcourir *en ordre inverse* la même suite d’états, en ayant en chacun d’eux des vitesses égales en valeur absolue, mais contraires en signe, à celles qu’il possédait au moment où, dans la première modification, il a traversé le même état. Cette faculté laissée aux systèmes que régissent les seules équations de la thermodynamique classique, faculté que les oscillations d’une pendule nous manifestent sous la forme la plus simple, est celle que Helmholtz désigne comme la capacité d’éprouver des *modifications réversibles*.”¹⁷

This invariance, or reversibility, does not occur in physical systems affected by “viscosity”, “friction” or “permanent transformations”. The mathematical terms corresponding to “these three classes of actions” change their sign when generalised “velocities” $\frac{d\alpha}{dt}, \dots, \frac{d\lambda}{dt}$ change their sign under time-symmetry. These physical systems are affected by time-irreversibility: this feature “differentiates deeply” them from purely mechanical systems. Duhem found that this deep difference represented an “insuperable hindrance” to reducing “complete thermodynamics ... to classic dynamics”.

How could be explained the presence of such terms in the equations of *motion*? Two alternatives were at stake: independent mathematical terms describing intrinsic features of the physical world, or fictitious terms roughly expressing the consequence of “*hidden motions*”. Duhem dismissed the second alternative, and therefore he was “forced to acknowledge” that “the fundamental equations of dynamics” are “more complex than Lagrange’s equations”. He looked upon his “doctrine” as a theoretical contribution to be placed in a conceptual stream recently established by Rankine. From that stream, which could be labelled *Energetics*, two main issues emerged: the intrinsic existence of dissipative effects, and the necessity of a more general science of transformations.

¹⁷ Duhem 1896a, p. 202.

“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.”¹⁸

In Duhem’s theory, Clausius’ inequality did not follow 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. Duhem’s theory would not have been overthrown by the opposite choice of “positive friction”. The fact that the hypothesis of negative work was in accordance with the experience, could not mean that subsequent experiences could not lead to a “contradiction”. Was the hypothesis of a positive work done by *dissipative forces* really odd? Duhem did not believe so: he pointed out the analogy between a hypothetical positive work and 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 le 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

¹⁸ Duhem 1896a, p. 205.

mécanique chimique ordinaire, irréalisables, hors de l'organisme, *dans les conditions de température où l'organisme fonctionne.*"¹⁹

Sciences of life suggested the possibility of a “new thermodynamics” or “*physiologic thermodynamics*”, which would satisfy le Principle of conservation of energy but would not “*the principle of the impossibility of perpetual motion*”. In the course of almost three centuries, most of the scientists had tried to reduce phenomena of life to mechanical actions. Duhem was showing another, complementary perspective: the study of phenomena occurring in living matter could have allowed 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 certaines 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 ?”²⁰

Duhem hinted at a mere possibility far from being fulfilled: at that time, the creative power of life was far outside the horizon of physics. Only after many decades, a few number of physicists and chemists would have tried to recollect Duhem’s heritage. Nowadays, for many other physicists, Duhem’s heritage is still outside the horizon of physics.

¹⁹ Duhem 1896a, p. 206.

²⁰ Duhem 1896a, p. 207.

Afterword

We can now wonder what heritage Duhem left to twentieth century physics. As far as I know, the most authoritative among contemporary physicists have never thought he had left a valuable heritage. Nevertheless something has survived, although in an unexpected way. Duhem's specific theoretical models and specific mathematical approach have not survived, but some important second-level and third-level issues have survived and found new implementations. Among them, I can list:

1. Physics and chemistry can be unified by a common mathematical framework, wherein chemical reactions are looked upon as generalised physical transformations;
2. Thermodynamics can transform into a generalised mechanics, in accordance with a generalisation of analytic mechanics;
3. physical reductionism should be overcome, in order to let physics account for the complexity of the real world.

With regard to the first issue, we can definitely say that specific analogies and specific mathematical machinery were dismissed in the subsequent developments of physics. Nevertheless, in the first decades of the twentieth century, some kind of unification between physics and chemistry through a generalisation a re-interpretation of analytic mechanics took really place. What we usually call Quantum Physics managed to describe the atomic structure and chemical bonds through a re-interpretation of Lagrangian and Hamiltonian formalism, at least in extremely simple configurations. This fact should not be overlooked: there is a structural analogy between Duhem's theoretical sketch put forward in 1896 and Schrödinger, Heisenberg and Jordan's re-interpretation of Hamilton's formalism. It is worth stressing that I am not talking about some kind of direct *influence* or something like that. I am talking about a new interpretation and a very different implementation of a similar second-level design. We could even assume an a-priori *incommensurability* between Duhem's 1896 theoretical

sketch and late 1920s Quantum Physics: indeed, with regard the first-level specific theoretical models, whatever kind of comparison would be meaningless.¹

In a season of history of physics wherein subtle meta-theoretical remarks on Quantum Physics were not at stake yet, the physicist and historian of physics Dugas was able to re-interpret Duhem's anti-atomism in a not-trivial way. Duhem did not rely on atoms as they were real *things*: in his view, atoms could only be considered as mere representations, not methodologically different from the mathematical models of continuous media, which Duhem relied on. This kind of abstract representation and methodological attitude was revived just by Quantum Physics.²

With regard to Duhem's second issue, the design of a generalized and fully mathematized Thermodynamics was accomplished by C.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 Thermodynamics had suffered a sharp split between the two traditions emerged in the first half: "the *FOURIER line*, which considered *workless dissipation*", on the one hand, and "*CARNOT line*, which considered *dissipationless work*", on the other. He noticed that, in the last decades of the nineteenth century, "thermodynamics was already regarded in Germany as a dead field, insusceptible of broadening or deepening". Apart from Planck, physicists confined themselves to equilibrium states and therefore thermodynamics resulted "inapplicable to *natural processes*", namely to real, irreversible phenomena.³

¹ It seems to me that R. Dugas managed to catch the deep connection between Quantum Physics and the tradition of Analytic Mechanics. 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 variable canoniques."

² 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 que 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."

³ Truesdell C. 1984, pp. 2, 7, 24-5.

According to Truesdell, Duhem represented an outstanding exception. Even though he appreciated Bridgmann efforts to cope with the foundation of Thermodynamics in the 1940s, he found that Bridgmann had “failed to reach the clarity, the definiteness, or the conceptual level maintained fifty years earlier by DUHEM”. Truesdell regretted that “DUHEM work had fallen into the general oblivion of classical mechanics in the interbellum”, although he acknowledged that “most of the work since 1960 follows the example of DUHEM”. He recommended that “DUHEM’s researches be studied until justice be done them”, and qualified the preface to his *Treatise on Energetics or General Thermodynamics* as a “program of modern rational thermodynamics”.⁴

Truesdell remarked that, before Duhem Thermodynamics was swinging between technology and cosmology: the operation of technical devices, 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”: he found that “its claims are often grandiose, its applications are usually trivial”. Furthermore, 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”.⁵

Truesdell’s aim was not different from Duhem’s: in Truesdell’s words, he was looking for “a thermodynamic theory formally similar to the classical one but vastly more general in scope”. The generalized Thermodynamics should “extend the concepts of mechanics so as to allow for diffusion and chemical reactions as well”.⁶

What Truesdell called “modern continuous 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 assumes

⁴ Truesdell C. 1984, p. 38, 40-1 and 45.

⁵ Truesdell C. 1984, pp. 59, 61-2. With regard to mathematics, he regretted that the reader had to face equations like $T \cdot dS \geq \delta Q$: “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 differential can be bigger than another, but even that a differential can be bigger than something which is not a differential.” (p. 61)

⁶ Truesdell C. 1984, p. 106.

$$S - S_0 \geq \int \frac{dq}{\vartheta} \Big|_{process},$$

“*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 is to deny “that there can be such a thing as a thermodynamics of irreversible processes”.⁷

With regard to the third issue, we find a sort of intellectual dialogue between Duhem and Poincaré in the treatise the latter devoted to Thermodynamics in 1892. 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*”. In the treatise on Thermodynamics he published in 1892, he claimed he would have built up “the whole structure of mathematical Physics only on Thermodynamics”. The complexity in 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 noticed that “the exact computation of the internal energy of a body depended on the state of external bodies”: the conservation of energy in a given body called into play “the whole universe”. A similar remark had to be extended to the second Principle, although it was express “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 even 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.⁸

Just like Duhem’s papers, essays and books, Poincaré treatise is a *treatise* in a very deep sense, for we find remarks on foundations of physics, meta-theoretical cogitations,

⁷ Truesdell C. 1984, pp. 123 and 157.

⁸ Poincaré H. 1892, pp. V, XII-XIII, and XVIII.

historical reconstructions, alongside detailed analysis of experiments, and comparisons between different interpretations of experiments. He appreciated Duhem researches, even though he devoted some pages of the treatise to oppose some interpretations of specific phenomena. In this context, the last passage of Poincaré *Préface* is quite meaningful.

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 méconnaissais 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.⁹

Poincaré Thermodynamics ranged over gases, fluids in motion, solids, saturated vapours, and sudden transformations 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”, “the temperature T is not uniform, and the integral in Clausius theorem loses its definite meaning”. He put forward a “general demonstration of Clausius theorem” when irreversibility took place, stemming from “heat exchanges with the sources”, but even from the system itself”. Although he found no difficulties in reducing “the principle of equivalence to the fundamental principles of mechanics”, for the second principle he found that “things are different”. He concluded that “irreversible phenomena and Clausius theorem cannot be explained by Lagrange equations”.¹⁰

In 1917, one year after Duhem death, E. Jouguet, *Ingénieur en chef des Mines*, and *Répétiteur à l'École Polytechnique*, published a paper in the *Revue générale des Sciences pures et appliquées*, wherein he gave a short account, and tried a comprehensive appraisal of Duhem contribution to theoretical physics. Jouguet had followed the tradition of French engineers who, in the second half of the nineteenth

⁹ Poincaré H. 1892, p. XIX. Poincaré objections to Duhem theory dealt with the entropy computation in a gaseous mixture, and the interpretation of Peltier effect: in particular, Poincaré criticised Duhem rejection of Maxwell conception of every electric current as a closed current. See *Ibidem*, pp. 321-38, 366-83, and 390.

¹⁰ See Poincaré H. 1892, pp. 98, 100, 103, 211-2, 392, and 422. He made extensively use of “Massieu characteristic functions”.

century, had steered French physics out of the arid lands of mere experimentalism. He could appreciate both Duhem physics and Duhem meta-theoretical commitments. He was aware that “Duhem had a very peculiar place in French science”: he had not taken part in the building up of “recent theories”, “his method contradicted some habits”, and 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”. At the end, however, an attentive reader could not be but struck by “wealth and originality” of Duhem’s scientific practice, which could be qualified as “very deep, mindful, and personal”.¹¹

Jouguet was aware that Duhem pathway to Thermodynamics had stemmed from the researches of Massieu, Gibbs and Helmholtz. The structural analogies Duhem had seen between “mechanical Statics” and “thermodynamics Statics” had not led him to develop 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. It was more a meta-theoretical commitment or a formal language than a definite content. That generalised mechanics was a science of motion in a general sense, or a science of transformations, according to the meaning of the word “motion” in peripatetic tradition. As Jouguet reported, “Mechanics and Thermodynamics were particular implementations of a single theoretical approach”: a unified science which dealt with “changes of state as well as changes of place”.¹²

Jouguet considered Duhem the founding father of the “thermodynamics of irreversible processes”: before his mathematical theories on “viscosity, friction, and hysteresis”, those phenomena had been taken seriously into account only “exceptionally”. Moreover, from “chemical Mechanics” new “differential equations of motion” in general sense stemmed, namely differential equations of the first order, corresponding

¹¹ 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 the history 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.

¹² Jouguet E. 1917, p. 41. Jouguet word I have translated into “theoretical approach” is “doctrine”. It seems to me that some nuances of the French word “doctrine” echo something meta-theoretical more than theoretical in the context of physics. On the other hand, translations like “tenet” or “belief” would seem to me slightly misleading.

to “variables without inertia”. Those equations, just like the equations of the ordinary mechanics, were “specific instances of the equations of Energetics”. In this sense, the Energetics encompassed different kinds of Mechanics, corresponding mathematically to different kinds of differential equations.¹³

Jouguet most interesting appraisal deals with the debated concept of “Mechanism”. He qualified Duhem as “mechanic”, but then he specified that “a mechanic should not identified with mechanical attitudes”. The statement sounds misleading unless we distinguish accurately between the two traditions emerged in the history of Mechanics: on the one hand, the specific mechanical models, on the other, the abstract mechanics. The former corresponded to what Duhem had qualified as “physical mechanics” in his 1903 book on the history of Mechanics, whereas the latter corresponded to what he had labelled “analytic mechanics”. Duhem mechanical approach was a *structural* Mechanism stemming from the latter tradition.¹⁴

In 1927, the physicist O. Manville, “chargé de conférence” at the faculty of Science at Bordeaux university, published an extensive book on Pierre Duhem physics. Two “Mémoire” closed the book: in the former, the mathematician Hadamard commented on Duhem as mathematician; in the latter, the historian A. Darbon commented on Duhem as historian. Manville analysis is quite detailed, and for many decades his book remained the sole study on Duhem theoretical physics. He pointed out that Duhem 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 understand “the real features of bodies” to be found underneath their “tangible aspect”.¹⁵

¹³ Jouguet E. 1917, pp. 43-5.

¹⁴ Jouguet E. 1917, pp. 48-50. It seems to me worth quoting some passages of Jouguet appraisal: “C’est dans l’Énergétique 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’Énergétique 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 une épanouissement du principe des vitesses virtuelles, sa Dynamique une extension du principe de D’Alembert et des équations de Lagrange.” (*Ibidem*, p. 50)

¹⁵ Manville O. 1927, pp. 18-9.

In part, Manville misunderstood the context of Duhem 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, wherein Thermodynamics was looked upon as “independent from whatever hypothesis on the nature of heat”, he associated Clausius, who had theorised on the mean free path of molecules. He rightly placed Duhem in the same pathway of Rankine, wherein “Rational Mechanics became a specific instance of a general Thermodynamics”. He found 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 “Carnot-Clausius principle” could be not exactly satisfied at 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 this “definition” of probability.¹⁶

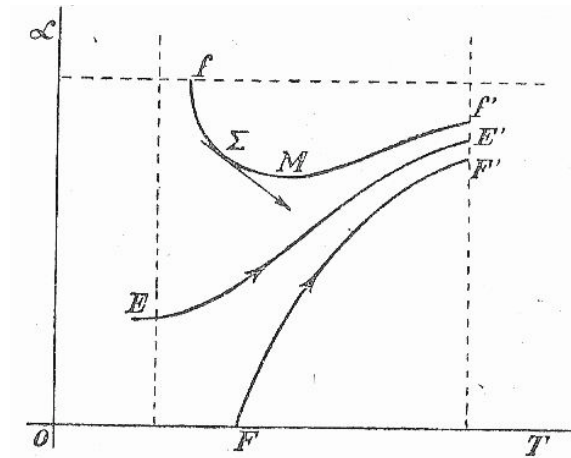
According to Manville, Duhem had managed to conflate “classic Dynamics” and the “Theory of conduction of heat”; at the same time, he had managed to explain why the two fields of physics “had evolved in an independent way”. Moreover, Duhem theory could exploit the cross-fertilisation between Thermodynamics and the theory of heat conduction: the latter had become “of great help in thermodynamics”. Manville remarks call into play the deepest structure of Duhem scientific enterprise, which can be synthesised into two logical stages. In the first stage, we find the unification between the mechanical theory of heat, wherein heat transformed into work without any conduction, and the theory of heat conduction, wherein there is conduction without any work. In the second stage, we find 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 physics appeared to Manville as “a chain whose ends” corresponded to “systems wherein *inertial actions* dominated”, and system wherein those actions could be neglected. In fact, among the new concepts emerged in Duhem theoretical physics, Manville mentioned the “*variables without*

¹⁶ Manville O. 1927, pp. 27 and 45-6, footnote 2 included.

inertia”, namely variables whose variations did not entail that the body “moves *locally*”.

17

Step by step, a hierarchy of complexity emerged, leading from “the simplest phenomena” to “the physics of *viscous media*”, then “systems with *friction*”, and eventually “systems with hysteresis”. Other new concepts emerged: the “*false equilibrium*”, or “an *infinite number of states of equilibrium* which classic Thermodynamics could not account for”, and the distinction between “*seeming viscosity*” and viscosity which “had to appear essentially and necessarily in the equations”. Manville managed to catch one of the most astonishing differences between Duhem generalised mechanics and “classic Mechanics”. In the space (α, T) of the parameters of the system, in the strip corresponding to states of false equilibrium, the velocity of the transformation $d\alpha/dt$ must vanish. This behaviour is quite different from that of a pendulum: it crosses the vertical line, which represents its state of equilibrium, “with *finite velocity*”, and does not remain there.



Moreover, in adiabatic transformations, on the boundaries of the strip of false equilibrium, when the derivative became less than a given value

$$\frac{d\alpha}{dt} = -\frac{C}{R_\alpha},$$

¹⁷ Manville O. 1927, pp. 66, 69, 75, and 90.

the system became “*instable*”, and a small increase of temperature made the system become “*explosive*”.¹⁸

Different kinds of irreversibility existed in physics, for different “abnormal branch 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*”. Although both of them dealt with irreversibility, in its nature hysteresis was quite different from “a *passive resistance*”. In systems submitted to permanent deformations, “an infinitely slow deformation could lead the system towards or back to a state of equilibrium”, differently from systems submitted to friction. If the first Principle of Thermodynamics, or “principle of Equivalence”, was still valid in the strange branch of hysteresis, the second Principle could not be applied, for reversible transformations were obviously excluded. Duhem had recourse to “the consequences of this principle as a mere hypothesis”. Manville acknowledged that Duhem had not manage to put forward a satisfactory theory for permanent deformations, even though he had tried to outline more sophisticated theories dealing with hysteresis in “*fast transformations*”, and “*the simultaneous existence of hysteresis and viscosity*”.¹⁹

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 Bridgmann approach to Thermodynamics were 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 Duhem scientific legacy had already become a sort of buried memory. The scientific community, which was becoming an international community, had focussed intellectual and material resources on sub-nuclear physics. Both the interest in the foundation of Thermodynamics, and the foundation of physics in general had progressively faded

¹⁸ Manville O. 1927, pp. 91, 93, 97, 110, 122, and 130.

¹⁹ Manville O. 1927, pp. 135-6, 154, 175, and 429.

away. The new theoretical physics was quite different from the wide-scope theoretical physics of the late nineteenth century.²⁰

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 commonly used”, involved only “operations which can be performed on the body *now*, and does not involve a knowledge of past history”. In general, there were “objects” which could not be “handled by the conventional thermodynamics”: he mentioned “the capricious freezing of a sub-cooled liquid”, and “atomic disintegration”.²¹

He regretted that “the two laws to which the physicists ascribes 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 whatever 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 logical link between entropy and “disorder” could not be easily bridged. He found that “this coupling is not always felicitous”, for “disorder” could not be looked upon as “a thermodynamic concept at all”.²²

He also found debatable that we could “assign a meaning simultaneously to flux of mechanical energy and flow of heat”. He noticed that, “in the case of small-scale turbulent motion in a liquid”, the two fluxes could not be clearly separated: the

²⁰ Bridgman mentioned “de Groot, Prigogine, and especially Onsager”. See Bridgman P.W. 1961, p. v. On the subsequent debate on the new trend in physics after the second World War, and on the re-emergence of interest in the complexity of the physical world, see Cocconi G. 1970, pp. 81-7, in particular pp. 83 e 87, Anderson P.W. 1972, 177, N. 4047, pp. 393-6, in particular pp. 393 e 395, and Schweber S. 1997, pp. 645-84, in particular pp. 659-71.

²¹ Bridgman P.W. 1961, pp. vi, 62, and 64.

²² 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 solidify 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)

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 well definite threshold separating micro from macro, or heat flux from flux of mechanical energy. The difficulty in disentangling microscopic from macroscopic motions also emerged in the measure of temperature, for “the thermometer must be at rest with regard to the system whose temperature is measured”. 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, “the external universe delivers mechanical work which the system receives as heat”.²³

We cannot leave Bridgman’s book before mentioning a meta-theoretical remark Duhem had stressed 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 the microscopic systems, which was just the kind of logical short-circuit Bridgman had already pointed out.²⁴

In 1950, the physicist and historian of physics R. Dugas acknowledged the role played by Duhem and Jouguet in his own scientific training and intellectual education. Duhem had developed the tradition of “Lagrange *analytic* 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”.²⁵

At the end, in Prigogine’s researches we find an exceptional re-interpretation of Duhem attempt at taming complexity. In 1947, in the essay *Etude Thermodynamique des Phénomènes irréversibles*, he pointed out “the deficiencies of classic

²³ Bridgman P.W. 1961, pp. 55, 67, 69, 72, 153, 192-3, and 231.

²⁴ Bridgman P.W. 1961, pp. 222-3.

²⁵ Dugas R. 1950, pp. 442-3.

thermodynamics”, and listed some of them. First of all, classic thermodynamics is “confined to states of equilibrium and reversible transformations”, and cannot account for chemical reactions, wherein the system is not in chemical equilibrium. Secondly, the two principles of classic Thermodynamics are confined to closed system, namely systems allowed to exchange energy but non matter with the external world. Other difficulties arose from the applications to electro-chemistry or to systems crossed by a temperature gradient. According to Prigogine, a more general Thermodynamics was required, in order to account for irreversible phenomena, states far from equilibrium and open systems.²⁶

Prigogine acknowledged explicitly the role played by Duhem in the setting up of a new Thermodynamics, even though his researches have not had the reception they deserved. The stress Duhem had put on Clausius’ “uncompensated heat” appeared to Prigogine a valuable contribution to a more general thermodynamics. This concept was tightly linked to the concept of entropy. Prigogine defined the entropy of a system as the sum of two contributions,

$$dS = \frac{dQ}{T} + \frac{dQ'}{T},$$

wherein dQ is the heat received from outside in the time dt , and dQ' is just Clausius’ uncompensated heat. The latter is developed in the course of irreversible processes taking place inside the system: it is therefore intrinsically positive. Even in the case of adiabatic transformations, where the system can exchange neither matter nor energy with the outside, we have $dS > 0$. In Prigogine picture, there are two different source of entropy: a “*transfer*” from outside and a “*production*” taking place inside.

$$dS = d_e S + d_i S$$

In its turn, the *transfer* of entropy in open systems is due to two different processes: transfer of heat and transfer of matter. Prigogine reminded the reader that all complex

²⁶ Prigogine I. 1947, pp. 3-5.

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”.²⁷

Prigogine found a sort of complementarity between Duhem’s third way 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”, and, at the same time, it offered a unifying framework for that field.²⁸

In the context of thermodynamics of irreversible processes, time could be looked upon as more than a mere “scalar” entity. Conversely, whenever “the flow of time plays an essential role”, Thermodynamics is at stake. This seemed quite natural to Prigogine. When we state that “there is always 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”.²⁹

When Prigogine outlined a general thermodynamics for “non-uniform systems”, he started from the analogy with the mechanics of continuous media. In particular he resumed “the classic equation of continuity of matter”

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho \omega_x)}{\partial x} + \frac{\partial(\rho \omega_y)}{\partial y} + \frac{\partial(\rho \omega_z)}{\partial z} = 0,$$

wherein ρ represented the density of the complex system in a given point at a given time, and ω represented its velocity. He assumed that the system consisted of a certain number “of different components”, that the components could experience chemical reactions, and that the different velocities of components could give rise to processes of diffusion.

²⁷ Prigogine I. 1947, pp. 1-3.

²⁸ Prigogine I. 1947, pp. 9-10.

²⁹ Prigogine I. 1947, p. 11.

Then he took into account a unspecified “extensive entity” F , of the same kind as mass or energy, and wrote down the variation over time of the quantity f , which was the density of F :

$$\frac{\partial f}{\partial t} = -\frac{\partial \Phi_x[F]}{\partial x} - \frac{\partial \Phi_y[F]}{\partial y} - \frac{\partial \Phi_z[F]}{\partial z} + \sigma[F].$$

In the right-hand side, Φ represents the flux of F , namely the quantity of F “entering the system” in unit time and surface, while $\sigma[F]$ represents the quantity of F “produced inside” in unit time and surface. We have in front of us the same mathematical structure, the same “local balance” put forward by Prigogine in the case of entropy.³⁰

For a set of components whose velocities are ω_γ Prigogine defined the centre of mass velocity

$$\vec{\omega} = \frac{1}{\rho} \sum_\gamma \rho_\gamma \vec{\omega}_\gamma,$$

and the “diffusion vector”

$$\vec{\Delta}_\gamma = \vec{\omega}_\gamma - \vec{\omega},$$

which is nothing else but “the excess of ω_γ with regard ω ”.

In the case of the “mass balance” we must define the two terms $\Phi[m_\gamma]$ and $\sigma[m_\gamma]$. While the former contains only the *mechanical* terms already defined, the latter deals with “the chemical reactions whose seat is the system itself”. In brief,

$$\Phi[m_\gamma] = \rho_\gamma \vec{\omega}_\gamma = \rho_\gamma \vec{\omega} + \rho_\gamma \vec{\Delta}_\gamma$$

³⁰ Prigogine I. 1947, pp. 76-9.

and

$$\sigma[m_\gamma] = \nu_\gamma M_\gamma \mathbf{V},$$

where ν_γ is “the stoichiometric coefficient”, M_γ “the molar mass”, and $\mathbf{V}$ the velocity of the chemical reaction.

In the end, the “mass balance” corresponded to the equation

$$\frac{\partial \rho_\gamma}{\partial t} + \sum_i \frac{\partial \rho_\gamma \omega^i}{\partial x_i} = - \sum_i \frac{\partial \rho_\gamma \bar{\Delta}_\gamma^i}{\partial x_i} + \nu_\gamma M_\gamma \mathbf{V}.$$

The sum over γ yielded the total balance of mass. Since chemical reactions do conserve the total mass of the system, $\sum_\gamma \nu_\gamma M_\gamma = 0$. Moreover, it is $\sum_\gamma \rho_\gamma \bar{\Delta}_\gamma = 0$, because of the meaning of $\bar{\Delta}_\gamma$. For the total mass of the system, the balance is therefore

$$\frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho \omega^i}{\partial x_i} = 0.^{31}$$

Prigogine deduced a similar equation for the “energy balance”, taking into account that, even in this case, $\sigma[U] = 0$. In brief

$$\frac{\partial u}{\partial t} = - \sum_i \frac{\partial}{\partial x_i} \left(u \omega^i + W^i + \sum_j P^{ij} \omega^j + \chi_o^i + \chi_d^i \right).$$

In the right-hand side, the first term correspond to “a convective flux of mass”, the second to “a caloric flux”, the third to “a flux linked to the pressure tensor”, the fourth to “a flux of potential energy”, and the last to “a flux of diffusion energy”.³²

³¹ Prigogine I. 1947, pp. 77-81.

³² Prigogine I. 1947, p. 80.

When he took into account the entropy balance, he first remarked that

$$\sigma[m]=0; \quad \sigma[U]=0; \quad \sigma[S]>0.$$

The final stage was not so easy to read:

$$\begin{aligned} \frac{\partial s}{\partial t} = & - \sum_i \frac{\partial}{\partial x_i} \left(s \omega^i + \frac{W^i}{T} + \frac{1}{T} \sum_\gamma \mu_\gamma^+ \rho_\gamma \Delta_\gamma^i \right) \\ & - \sum_i \left(\frac{W^i}{T^2} \frac{\partial T}{\partial x_i} + \frac{\omega^i}{T} \frac{\partial p}{\partial x_i} + \frac{1}{T} \sum_\gamma \rho_\gamma \Delta_\gamma^i \frac{\partial \mu_\gamma^+}{\partial x_i} \right) + \frac{A \mathbf{V}}{T} + \frac{\sigma[E]}{T}. \end{aligned}$$

In the right-hand side of the equation, the first sum represents the flux: the three terms correspond to “the convective entropic flux”, “the reduced caloric flux”, and “the entropic flux due to diffusion”. The other terms represent the different sources of entropy production. The second sum contains three terms corresponding to “non-uniformity of intensive variables T , p , and μ^+ ”, where μ^+ is Gibbs’ “chemical molar potential” for unit mass. The last two terms correspond to “the presence of chemical reaction” and “the degradation of nobler kinds of energy into internal energy” of the system.

To sum up, entropy production was linked to both “transport phenomena (thermal conductivity, viscosity, and diffusion) and chemical reactions”. Prigogine remarked that, in his equation, the centre of mass velocity ω did not appear, even though its spatial derivatives did. The global motion of the system did not contribute to the production of entropy: it corresponded to “a *reversible phenomenon*”.³³

In the last chapter he went back to the relationship between thermodynamics and time: he faced the issue in a very radical way. Starting from Eddington’s remark on the relationship between the time flow and ds/dt , Prigogine tried to define “a new scale of time” linked to “the production of entropy”. The thermodynamics of irreversible

³³ Prigogine I. 1947, pp. 95-9. See also p. 20 for the relationship between entropy and Gibbs’ molar potential.

phenomena would have allowed physicists to compute “the duration of a phenomenon by means of its *content of irreversibility*”. We therefore have in front of us two kinds of time: the well-known astronomical time t , and the time τ stemming from the production of entropy $\sigma[S]$.³⁴

He assumed that

$$\tau_0 = t_0,$$

and that, starting from τ_0 , τ grew with the growth of t . In other words,

$$\frac{d\tau}{dt} > 0.$$

Other specific assumptions allowed Prigogine to handle the demanding and slippery subject matter. Firstly

$$\sigma[S_\tau] d\tau = \sigma[S_t] dt,$$

then

$$\sigma[S_\tau] = \alpha \text{ (constant),}$$

and finally

$$\left(\frac{d\tau}{dt} \right)_{t=t_0} = 1.$$

³⁴ Prigogine I. 1947, p. 133.

This means that, at the first order, $(d\tau)_{t=t_0} = (dt)_{t=t_0}$, and that $\sigma[S_{t_0}] = \alpha$. Therefore the relationship between τ and t becomes

$$\frac{d\tau}{dt} = \frac{\sigma[S_t]}{\sigma[S_\tau]} = \frac{\sigma[S_t]}{\alpha} = \frac{\sigma[S_t]}{\sigma[S_{t_0}]}.$$

This is a differential equation which can be solved when we know, or are able to make a reasonable assumption about, the function $\sigma[S_t]$.³⁵

For chemical reactions approaching the equilibrium, the literature offered to Prigogine a function of the kind

$$\frac{d\tau}{dt} = \frac{\sigma[S_t]}{\sigma[S_{t_0}]} = e^{-2b(t-t_0)},$$

where b is a constant. A simple integration yielded

$$\tau - \tau_0 = \frac{1}{2b} \left[1 - e^{-2b(t-t_0)} \right].$$

At the first order, for t close to t_0 ,

$$\tau - \tau_0 = (t - t_0) - b(t - t_0)^2. \quad ^{36}$$

In this specific case,

$$\frac{d^2\tau}{dt^2} = -2be^{-2b(t-t_0)} < 0.$$

³⁵ Prigogine I. 1947, pp. 133-4.

³⁶ Prigogine I. 1947, pp. 134-5.

Prigogine assumed that, in general,

$$\frac{d^2\tau}{dt^2} = \frac{1}{\sigma[S_{t_0}]} \frac{d\sigma[S_t]}{dt} < 0,$$

when “the system approach a state of equilibrium or a stationary state” after an initial perturbation. He chose a more general kind of function decreasing over time,

$$\sigma[S_t] = \alpha_0 + \frac{\alpha_1}{t + \beta} + \frac{\alpha_2}{(t + \beta)^2} + \dots,$$

and therefore the differential equation became

$$\frac{d\tau}{dt} = \frac{\alpha_0}{\sigma_0} + \frac{\alpha_1}{\sigma_0} \frac{1}{t + \beta} + \frac{\alpha_2}{\sigma_0} \frac{1}{(t + \beta)^2} + \dots$$

Another simple integration yielded

$$\tau = t_0 + \frac{\alpha_0}{\sigma_0} (t - t_0) + \frac{\alpha_1}{\sigma_0} \log \frac{t + \beta}{t_0 + \beta} + \frac{\alpha_2}{\sigma_0} \frac{t - t_0}{(t + \beta)(t_0 + \beta)} + \dots$$

When the system approaches equilibrium, $\sigma[S_t] \rightarrow 0$ for $t \rightarrow \infty$. In such a case, we can retain only the term

$$\sigma[S_t] = \frac{\alpha_1}{t + \beta}.$$

In the simple case wherein $\beta = 0$,

$$\tau = t_0 + t_0 \log \frac{t}{t_0}.^{37}$$

Independently from the specific law connecting astronomical time to thermodynamic time, two remarks can be made: the two *time* are different, and the function connecting them could be non-linear. Although the chain of assumptions and approximations built up in the course of the deduction is questionable, Prigogine managed to show that a new, different definition of time could be put forward. We are really dealing with 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, namely the quasi-regular motion of sun and planets. Nevertheless, thermodynamic time would have a wider scope, for it spans physics, chemistry, and perhaps the sciences of life. Moreover, we could even assume the existence of a plurality of *time*: we could look for the most suitable *time* to be associated to every kind of phenomena.

Prigogine remarked that thermodynamic time could suit the living beings: indeed, metabolic processes “are the seats of irreversible phenomena”. We are here facing a sort of Aristotelian concept time: time as a complex entity, far from the abstract, purified concept emerged together with the modern science. Prigogine time is more a physical than an algebraic entity. It is a “*local*” time, for it “is generated by the irreversible processes taking place in a well definite space”. Nevertheless, the thermodynamic time could aspire to a different kind of generality. Differently from the astronomical time, which is only the component of a four-vector, it stems from the entropy, which is a relativistic invariant.³⁸

After some years, Prigogine published a book in English, which was intended as a first systematization of the same subject matter: the thermodynamics of irreversible processes. The book seemed triggered off by the fact that, at that time, the theory had already led to “a large number of applications”. In the “Preface”, Prigogine reminded the reader that “a serious limitation of classic thermodynamics” stood in its narrow scope: “reversible processes” and “true equilibrium states”. On the other hand, “the majority of phenomena” in the fields of astrophysics, meteorology, geology and biology

³⁷ Prigogine I. 1947, pp. 135-6.

³⁸ Prigogine I. 1947, pp. 136-8.

dealt with “irreversible processes which take place outside the equilibrium state”. From the mathematical point of view, reversible processes are 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 are expressed mathematically, for instance, by “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 is invariant under the transformation $t \rightarrow -t$, the latter is not. Such equation broke the symmetry between past and future, which was a fundamental feature of mechanics.³⁹

Another generalisation involved the links between a system and the surrounding environment. If *isolated* systems can exchange neither matter nor energy, and *closed* systems can exchange only energy, *open* systems can “exchange both energy and matter with the exterior”. Open systems were the kind of systems more suitable to represent the complexity of phenomena spanning all sciences of nature from physics to 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”. This split had already put forward by Prigogine in 1947, and applied to entropy, mass and energy. In a system composed of many chemical compounds γ , the variation of the mass m_γ can therefore be written

³⁹ Prigogine I. 1955, pp. V-VI, and 14.

$$dm_\gamma = d_e m_\gamma + d_i m_\gamma = d_e m_\gamma + M_\gamma \sum_{\rho=1}^r \nu_{\gamma\rho} d\xi_\rho ,$$

where M_γ is the molar mass of the chemical compound γ , $\nu_{\gamma\rho}$ “the stoichiometric coefficient of γ ” in every chemical reaction, and ξ “the degree of advancement or extent of reaction”. The variable ξ is linked to the “chemical reaction rate” v by the equation

$$v = \frac{d\xi}{dt} .^{40}$$

In the context of natural sciences, Prigogine stressed the importance of “stationary non-equilibrium states”. Since they are not equilibrium states, the entropy production is different from zero, but the variables describing the system do not depend on time, since the state is stationary. In this case,

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt} = 0 .$$

As

$$\frac{d_i S}{dt} > 0 ,$$

we “necessarily have”

$$\frac{d_e S}{dt} < 0 .$$

⁴⁰ Prigogine I. 1955, pp. 3-7.

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 sending out entropy towards the environment, therefore increasing the entropy of the environment. When the system is the seat of chemical reactions, the stationary state can realize a sort of “coupling between transport phenomena and chemical reaction”. Prigogine emphasised the importance of phenomena of this kind in “biological processes”. He believed that the thermodynamics of irreversible phenomena taking place in open systems could really allow scientists to better understand life.⁴¹

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*”.⁴²

A striking instance was offered by “Bénard instability”, wherein ordered convective streams emerged in a liquid layer submitted to a “sufficiently large” gradient of temperature. Although the “entropy production” increases, the layer can be found “in a state of organization” higher than the state of rest. Contrary to what expected on 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 great fluctuations “stabilized by exchanges of energy with the outside world”.⁴³

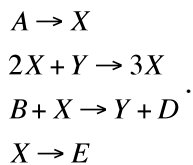
⁴¹ Prigogine I. 1955, pp. 74, 82, and 89. See also p. 91: “The behaviour of living organisms has always seemed so strange from the point of view of classical thermodynamics that the applicability of thermodynamics to such systems has often been questioned. One may say that from the point of view of the thermodynamics of open and stationary systems a much better understanding of their principal features is obtained.”

⁴² Prigogine I. 1977, pp. 263-4. Prigogine won the Nobel Prize for Chemistry in 1977.

⁴³ Prigogine I. 1977, p. 267.

Prigogine stressed that far from equilibrium the behaviour of a physical system “may become very specific”, whereas “[t]he laws of equilibrium are universal”. The state of the system can experience bifurcations: little changes in the initial state give place to ample fluctuations which lead the system to sudden transition towards stable or instable “branches”.

These 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 can be represented by

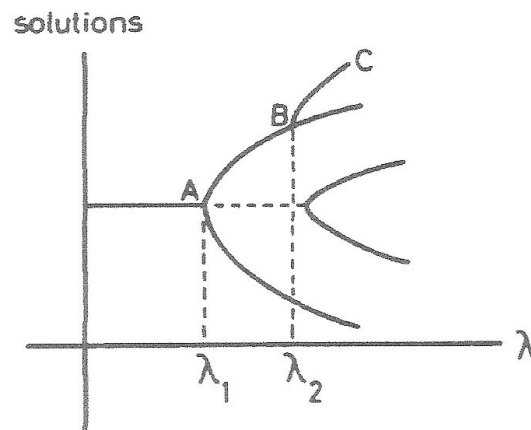


The concentrations of “the initial and final products” A , B , C , D , “are maintained constant”, whereas “the two intermediate components, X , Y , may change in time”. The process is described by the non-linear differential equations

$$\begin{aligned} \frac{dX}{dt} &= A + X^2Y - BX - X \\ \frac{dY}{dt} &= BX - X^2Y \end{aligned} \quad .^{44}$$

When we increase the value of a parameter λ , like the concentration B “in the Brusselator scheme”, multiple solutions of the system of differential equations appear. The picture inserted in Prigogine paper shows that there is “a single solution for λ_1 , but multiple solutions for the value λ_2 ”.

⁴⁴ 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 Prigogine I. and Stengers I. 1986, pp. 223-8.



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”.⁴⁵

⁴⁵ Prigogine I. 1977, p. 273.

BIBLIOGRAPHY

- Anderson P.W. 1972, "More Is Different", *Science*, 177, N. 4047, pp. 393-6.
- Badino M. 2005, "Ludwig Boltzmann e l'alba della probabilità in fisica", in Boltzmann L. 2005, pp. 11-85.
- Balian R. 1992, *From Microphysics to Macrophysics*, Springer, Berlin.
- Baracca A. and Rossi A. 1978 (eds.), *Materia e energia : antologia di testi*, Feltrinelli, Milano.
- Berthelot M. 1894, "Le principe du travail maximum et l'entropie", *Comptes Rendus de l'Académie des Sciences*, Gauthier-Villars, Paris, 118, pp. 1378-92.
- Bevilacqua F. 1993, "Helmholtz's Ueber der Erhaltung der Kraft – The Emergence of a Theoretical Physicist", in Cahan D. (ed.) 1993a, pp. 432-59.
- Bierhalter G. 1993, "Helmholtz's Mechanical Foundation of Thermodynamics", in Cahan D. (ed.) 1993a, pp. 291-333.
- Boltzmann L. 1872, "Weiteren Studien über das Wärmegleichgewicht unter Gasmolekülen", in Boltzmann L. 1909, I. Band, pp. 317-402.
- Boltzmann L. 1877a, "Bemerkungen über einige Probleme der mechanischen Wärmetheorie", in Boltzmann L. 1909, II. Band, pp. 112-48.
- Boltzmann L. 1877b, "Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht", in Boltzmann L. 1909, II. Band, pp. 164-223.
- Boltzmann L. 1886, "The second Law of Thermodynamics", in Boltzmann L. 1974, pp. 13-32.
- Boltzmann L. 1890, "On the significance of theories", in Boltzmann L. 1974, pp. 33-6.
- Boltzmann L. 1892, "On the methods of theoretical physics", in Boltzmann L. 1974, pp. 5-12.
- Boltzmann L. 1896, "Zur Energetik", *Annalen der Physik und Chemie*, 58, pp. 595-8.
- Boltzmann L. 1897a, "On the indispensability of atomism in natural science", in Boltzmann L. 1974, pp. 41-53.

- Boltzmann L. 1897b, "More on atomism", in Boltzmann L. 1974, pp. 54-6.
- Boltzmann L. 1899, "On the Development of the Methods of theoretical Physics in recent Times", in Boltzmann L. 1974, pp. 77-100.
- Boltzmann L. 1905, "The Relations of Applied Mathematics", in Rogers H.J. (ed.) 1905, *Congress of Arts and Science, St. Louis 1904*, vol. I, Houghton, Mifflin and C., Boston and New York, pp. 591-603.
- Boltzmann L. 1909, *Wissenschaftlichen Abhandlungen*, Barth, Leipzig,
- Boltzmann L. 1974, *Theoretical Physics and Philosophical Problems*, (McGuinness B. ed.) D. Reidel Publishing Company, Dordrecht-Holland/Boston-U.S.A.
- Boltzmann L. 2005, *Fisica e probabilità*, Edizioni Melquiades, Milano.
- Bordoni S. 2008, *Crossing the boundaries between matter and energy*, Università degli Studi di Pavia/ La Goliardica Pavese, Pavia.
- Bordoni S. 2008, *Crossing the boundaries between matter and energy*, Università degli Studi di Pavia/ La Goliardica Pavese, Pavia.
- Brenner A. 1990, *Duhem Science réalité et apparence*, Vrin, Paris.
- Brenner A. 1992, "Introduction", in Duhem 1992, pp. XI-XXI.
- Bridgman P.W. 1961, *The Nature of Thermodynamics*, Harper & Brothers, New York.
- Broglie (de) L. 1964, *La Thermodynamique de la particule isolée*, Gauthier-Villars, Paris.
- Brouzeng P. 1981, *L'oeuvre scientifique de Pierre Duhem et sa contribution au développement de la thermodynamique des phénomènes irréversibles*, (2 vols.), These (pour obtenir le grade de Docteur d'Etat ès Sciences), Université de Bordeaux I.
- Brouzeng P. 1987, *Duhem 1861-1916 – Science et Providence*, Belin, Paris.
- Brush S. G. 1976, *The Kind of Motion we call Heat*, Books 1 and 2, North Holland Publishing Company, Amsterdam-New York-Oxford.
- Brush S. G. 1978, *The Temperature of History*, Burt Franklin & Co., New York.
- Brush S.G., Everitt C.W.F., and Garber E. (eds.) 1986a, *Maxwell on Molecules and Gases*, The MIT Press, Cambridge Massachusetts – London England.
- Brush S.G., Everitt C.W.F., and Garber E. 1986b, "Preface" to Brush S.G., Everitt C.W.F. and Garber E. (eds.) 1986a, pp. xvii-xxvii.

Brush S.G., Everitt C.W.F., and Garber E. 1986c, "Kinetic Theory and the Properties of Gases: Maxwell's Work in Its Nineteenth-Century Context", in Brush S.G., Everitt C.W.F. and Garber E. (eds.) 1986a, pp. 3-63.

Buchwald J.Z. 1985, *From Maxwell to Microphysics*, University of Chicago Press, Chicago.

Buchwald J.Z. 1993, "Electrodynamics in Context – Object States, Laboratory Practice, and Anti-Romanticism", in Cahan D. (ed.) 1993a, pp. 335-73.

Bui D. 2003, *Aspects de la genèse et du développement des idées épistémologiques de Pierre Duhem*, Thèse de Doctorat, Université de Genève, Faculté des Lettres – Département de philosophie – Unité d'histoire et philosophie de la science.

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

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

Cantor G.N. and Hodges M.J.S. (eds.) 1981, *Conceptions of ether – Studies in the history of ether theories 1740-1900*, Cambridge University Press, Cambridge/ London/ New York.

Cardwell D.S.L. 1971, *From Watt to Clausius*, Cornell University Press, Cornell (New York).

Cassirer E. 1936, *Determinismus und Indeterminismus in der modernen Physik*, Wettergren & Kerbers Förlag, Göteborg.

Cassirer E. 1950, *The Problem of Knowledge – Philosophy, Science, and History since Hegel*, Yale University Press, New Haven.

Clausius R. 1857, "Ueber die Art der Bewegung, welche wir Wärme nennen", *Annalen der Physik* 100, p. 353-79.

Clausius, R. 1862, "Über die Wärmeleitung gasförmiger Körper", *Annalen der Physik* 115, pp. 1-57.

Clausius, R. 1864, *Abhandlungen über die Mechanische Wärmetheorie*, Electronic manuscript from the Bibliothèque nationale de France.

Cocconi G. 1970, *The Role of Complexity in Nature*, in Conversi M. (ed.) *Evolution of Particle Physics*, Academic Press Inc., New York, pp. 81-7,

Cohen I.B. 198, *Revolution in Science*, Harvard University Press, Cambridge (Massachusetts).

D'Agostino S. 2000, *A History of the Ideas of the Theoretical Physics – Essays on the Nineteenth and Twentieth Century Physics*, Boston Studies in the Philosophy of Science, Kluwer Academic Publishers, Dordrecht/ Boston/ London.

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

Dugas R. 1950, *Histoire de la Mécanique*, Editions du Griffon, Neuchatel.

Dugas R. 1959, *La théorie physique au sens de Boltzmann*, Éditions du Griffon, Neuchatel-Suisse .

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

Duhem P. 1888, *Sur l'aimantation par influence*, Thèse présentée à la Faculté des Sciences de Paris, le 30 octobre 1888, pour obtenir le grade de Docteur en Sciences mathématiques.

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

Duhem P. 1892a, “Commentaire aux principes de la Thermodynamique- Première partie”, *Journal de Mathématiques pures et appliquées*, 4^e série, tome VIII, p. 269.

Duhem P. 1892b, “Quelques réflexions au sujet des théories physiques”, *Revue des questions scientifiques*, 31, pp. 139-77; reprinted in Duhem P. 1987, pp. 1-39.

Duhem P. 1893a “Commentaire aux principes de la Thermodynamique – Deuxième partie”, *Journal de Mathématiques pures et appliquées*, 4^e série, tome IX, p. 293.

Duhem P. 1893b, *Introduction à la mécanique chimique et à la théorie des phénomènes électriques*, Ad. Hoste, Gand.

Duhem P. 1893c, “Une nouvelle théorie du monde inorganique”, *Revue des questions scientifiques*, 33, pp. 90-133; reprinted in Duhem P. 1987, pp. 40-83.

Duhem P. 1893d, “Physique et métaphysique”, *Revue des questions scientifiques*, 34, pp. 55-83; reprinted in Duhem P. 1987, pp. 84-112.

Duhem P. 1893e, “L’école anglaise et les théories physiques, à propos d’un livre de W. Thomson”, *Revue des questions scientifiques*, 34, pp. 345-78; reprinted in Duhem P. 1987, pp. 113-46.

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

Duhem P. 1894b, “Sur les déformations permanentes et l’hystérésis”, *Mémoires présentées par divers savants étrangers et Mémoires couronnées par l’Académie de Belgique*, Classe des Sciences, tome LIV, 13 octobre 1894.

Duhem P. 1894c, “Quelques réflexions au sujet de la physique expérimentale”, *Revue des questions scientifiques*, 36, pp. 179-229; reprinted in Duhem P. 1987, pp. 147-97.

Duhem P. 1895a, “Sur les déformations permanentes et l’hystérésis - Deuxième mémoire : les modifications permanentes du soufre”, *Mémoires présentées par divers savants étrangers et Mémoires couronnées par l’Académie de Belgique*, Classe des Sciences, tome LIV, 11 mars 1895.

Duhem P. 1895b, “Sur les déformations permanentes et l’hystérésis – troisième mémoire : Théorie générale des modifications permanentes”, *Mémoires présentées par divers savants étrangers et Mémoires couronnées par l’Académie de Belgique*, Classe des Sciences, tome LIV, 3 août 1895.

Duhem P. 1895c, *Les théories de la chaleur*, in Duhem 1992, pp. 351-441.

Duhem P. 1896a, “Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques”, *Mémoires de la Société des Sciences physiques et naturelles de Bordeaux*, 5^e série, tome II.

Duhem P. 1896b, “L’évolution des théories physiques du XVII^e siècle jusqu’à nos jours”, *Revue des questions scientifiques*, 40, pp. 463-99; reprinted in Duhem P. 1987, pp. 198-234.

Duhem P. 1903, *L’évolution de la mécanique*, in Duhem 1992, pp. 1-348.

Duhem P. 1906, *La Théorie Physique, son objet et sa structure*, Chevalier et Riviera, Paris.

Duhem P. 1987, *Prémices philosophiques*, (présenté avec une introduction en anglais par S. L. Jaki), Brill, Leiden/ New York/ København/ Köln.

Duhem P. 1992, *L'évolution de la mécanique* – suivi de « Les théories de la chaleur », « Analyse de l'ouvrage de Ernst Mach : La Mécanique », Librairie philosophique J. Vrin, Paris.

Feyerabend P.K. 1970, “Consolations for the Specialist”, in Lakatos I. and Musgrave A. (eds.) 1970, *Criticism and the Growth of Knowledge*, Cambridge University Press, Cambridge UK, pp. 197-230

FitzGerald G.F. 1896, “Ostwald's energetics”, *Nature*, LIII, pp. 441-2.

Fourier J. 1822, *Théorie analytique de la chaleur*, Didot, Paris.

Galison P. 2003, *Einstein's Clocks, Poincaré's Maps – Empires of Time*, Norton & Company, New York/ London.

Giannetto E. 1995, “Physical Theories and Theoretical Physics”, in Rossi A. (ed.) 1995, *Atti del XIII Congresso Nazionale di Storia della Fisica*, Conte, Lecce, pp. 163-7.

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

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

Giordano G. 2005, *La filosofia di Ilya Prigogine*, Siciliano, Messina.

Gembillo G., Giordano G, and Stramandino F. 2004, *Ilya Prigogine scienziato e filosofo*, Siciliano, Messina.

Harman P.M. 1892, *Energy, Force and Matter. The Conceptual Development of Nineteenth-Century Physics*, Cambridge University Press, Cambridge/ London/ New York.

Heaviside O. 1893, *Electromagnetic Theory*, The Electrician Printing and Publishing Company Limited, London.

Helm G. 1895, “Zur Energetik“, *Annalen der Physik und Chemie* 57, pp. 646-59.

Helm G. 1898, *Die Energetik nach ihrer geschichtlichen Entwicklung*, Verlag von Veit & Comp., Leipzig; reprinted in Helm G. 1981, *Die Energetik*, Arno Press, New York.

Helmholtz H. 1882, "Die Thermodynamik Chemischer Vorgänge", *Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin*, (2 Febr. 1882) vol. I. pp. 22-39; in Helmholtz H. 1883, pp. 958-78.

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

Hertz H. 1892, *Untersuchungen über die Ausbreitung der elektrischen Kraft*, Barth, Leipzig; English translation in Hertz H. 1962, *Electric Waves*, Dover, New York.

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

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

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

Jouguet E. 1909, *Lectures de Mécanique, Deuxième partie – l'organisation de la Mécanique*, Gauthier-Villars, Paris.

Jouguet E. 1917, "L'œuvre scientifique de Pierre Duhem", in *Revue générale des Sciences pures et appliquées*, Paris, pp. 40-9.

Klein M.J., "The scientific Style of Josiah Willard Gibbs", in Aris R., Davies H.T. e Stuewer R. (eds.) 1983, *Springs of scientific creativity – Essays of Founders of Modern Science*, University of Minnesota Press, Minneapolis.

Kragh H. 1993, "Between Physics and Chemistry: Helmholtz's Route to a Theory of Chemical Thermodynamics", in Cahn D. (ed.) 1993, pp 403-31.

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

Kuhn T.S. 1996, *The Structure of Scientific Revolutions*, The University of Chicago Press, Chicago/ London.

Lami E.O. (ed.) 1881-91, *Dictionnaire encyclopédique et biographique de l'Industrie et des Arts Industrielles 1881-1891*, 9 vols, Librairie des Dictionnaires, Paris.

Larmor J. 1987, "A Dynamical Theory of the Electric and Luminiferous Medium, part III: Relations with Material Media", *Philosophical Transactions of the Royal Society*, 190, pp. 205-300.

Lowiger A. 1967, *The Methodology of PIERRE DUHEM*, AMS Press, New York.

Maiocchi R. 1985, *Chimica e filosofia – Scienze, epistemologia, storia e religione nell'opera di Pierre Duhem*, La Nuova Italia, Firenze.

Manville O. 1927, *L'oeuvre scientifique de Pierre Duhem*, Feret et fils, Bordeaux

Martin R.N.D. 1991, *PIERRE DUHEM – Philosophy and History in the Work of a Believing Physicist*, Open Court, La Salle (Illinois).

Massieu F. 1869a, "Sur les Fonctions caractéristiques des divers fluides", *Comptes Rendus de l'Académie des Sciences* LXIX, pp. 858-62.

Massieu F. 1869b, "Addition au précédent Mémoire sur les Fonctions caractéristiques", *Comptes Rendus de l'Académie des Sciences* LXIX, pp. 1057-61.

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

Maxwell J.C. 1860, "Illustrations of the Dynamical Theory of Gases"; reprinted in Maxwell J.C. 1890, vol. 1, pp. 377-409.

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

Maxwell J.C. 1873, "Molecules", *Nature*, 8, pp. 437-41.

Maxwell J.C. 1875, "Atom", ninth edition of *Encyclopaedia Britannica*; in Maxwell J.C. 1890, vol. 2, pp. 445-84.

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

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

Ostwald W. 1895a, "La déroutte de l'atomisme contemporain", *Revue générale des Sciences pures et appliquées*, 21, pp. 953-8.

Ostwald W. 1895b, “Lettre sur l'énergétique“, *Revue générale des Sciences pures et appliquées*, 21, pp. 1069-71.

Ostwald W. 1896, “Zur Energetik“, *Annalen der Physik und Chemie* 58, pp. 154-67.

Perrot, P. 1998, *A to Z of Thermodynamics*, Oxford University Press, Oxford and New York

Planck M. 1896, “gegen die neuere Energetik“, *Annalen der Physik und Chemie*, 57, pp. 72-8.

Poincaré H. 1889, *Leçons sur la Théorie Mathématique de la lumière, Cours de Physique Mathématique*, G. Carré, Paris.

Poincaré H. 1890, *Électricité et Optique, Cours de Physique Mathématique*, G. Carré, Paris.

Poincaré H. 1892, *Thermodynamique, Cours de Physique Mathématique*, G. Carré, Paris.

Poincaré H. 1893, “Le mécanisme et l'expérience“, *Revue de Métaphysique et de Morale*, Hachette, Paris, pp. 534-7.

Poynting J.H. 1885, “On the connection between Electric Current and the Electric and Magnetic Induction in the surrounding field“, *Philosophical Transactions of the Royal Society*, 176, pp. 277-306.

Prigogine I. 1947, *Etude Thermodynamique des Phénomènes Irréversibles*, Dunod, Paris/ Desoer, Liège.

Prigogine I. 1955, *Thermodynamics of Irreversible Processes*, Charles C Thomas, Springfield (Illinois).

Prigogine I. 1962, *Non-Equilibrium Statistical Mechanics*, John Wiley & Sons, New York/ London.

Prigogine I. 1977b, “Time, structure and fluctuations“, in Frängsmyr T. and Forsén S. (eds.), Nobel lectures, Chemistry 1971-1980, World Scientific Publishing Co., Singapore, 1993, pp. 263-85. See also http://nobelprize.org/nobel_prizes/chemistry/laureates/1977/prigogine-lecture.html

Prigogine I. 2008, *Les lois du chaos*, Flammarion, Paris.

Prigogine I. and Nicolis G. 1977, *Self-Organisation in Nonequilibrium Systems*, John Wiley & Sons, New York/ London/ Sydney/ Toronto.

Prigogine I. and Stengers I. 1986, *La nouvelle alliance*, Gallimard, Paris.

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

Rankine W.J.M. 1853, “On the Mechanical Action of Heat”, Section VI, in Rankine W.J.M. 1881, pp. 310-38.

Rankine W.J.M. 1855, “Outlines of the Science of Energetics”, in Rankine W.J.M. 1881, pp. 209-28.

Rankine W.J.M. 1867, “On the Phrase ‘Potential Energy’, and on the Definitions of Physical Quantities”, in Rankine W.J.M. 1881, pp. 229-33.

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

Redondi P. 1978, *Epistemologia e storia della scienza – Le svolte teoriche da Duhem a Bachelard*, Feltrinelli Editore, Milano.

Reech F. 1851, “Notice sur un Mémoire intitulé : Théorie de la force motrice du calorique “, *Comptes Rendus de l’Académie des Sciences*, pp. 567-71.

Reech F. 1854, *Théorie générale des effets dynamiques de la chaleur*, Mallet-Bachelier, Paris.

Reech F. 1856, “Récapitulation très-succinte des reserches algébriques faites sur la théorie des effets mécaniques de la chaleur par différents auteurs“, *Journal de Mathématiques pures et appliquées*, pp. 58-75.

Renn J. and Rauchhaupt U. 2005, “In the Laboratory of Knowledge”, in Renn J. 2005 (ed.), *Albert Einstein chief engineer of the universe – One hundred authors for Einstein*, Wiley-Vch, Weinheim, and Max Planck Institute for the History of Science, Berlin.

Ross S. 1962, “Scientist: the story of a word”, *Annals of Science* 18, pp 65-86.

Sainte-Claire Deville H. 1894, “Observations sur une Communication de M. Wurtz relative à la chaleur de combinaison de l’hydrate de chloral“, *Comptes Rendus de l’Académie des Sciences*, 90, pp. 341-2.

Schweber S. 1997, *A Historical Perspective on the Rise of the Standard Model*, in Hodeson L., Brown L., Riordan M., and Dresden M. (eds.), *The Rise of the Standard Model*, Cambridge University Press, Cambridge, pp. 645-84.

Stein H. 1981, “‘Subtler forms of matter’ in the period following Maxwell”, in Cantor G.N. and Hodges M.J.S. (eds.) 1981, pp. 309-40.

Stengers I. 2003, *Cosmopolitiques I* (1-2-3), La Découverte, Paris.

Stoffel J-F. 2002, *Le phénoménalisme problématique de Pierre Duhem*, Académie Royale de Belgique, Bruxelles.

Truesdell C.A. 1980, *The tragicomical history of thermodynamics 1822-1854*, Springer-Verlag, New York/Heidelberg/Berlin.

Truesdell C. 1984, *Rational Thermodynamics*, Springer-Verlag, New York/ Berlin/ Heidelberg/ Tokio.

Truesdell C. 1986, “What Did Gibbs and Carathéodory Leave Us About Thermodynamics?”, in Serrin J. (ed.) 1986, *New Perspectives in Thermodynamics*, Springer-Verlag, Berlin/ Heidelberg/ New York/ Tokio, pp. 101-24.

Truesdell C. and Bharatha S. 1977, *Classical Thermodynamics as a Theory of Heat Engines*, Springer-Verlag, New York / Heidelberg/ Berlin.