

# From thermodynamics to philosophical tradition: Pierre Duhem's research between 1891 and 1896

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**Abstract** In the few years 1891–1896, the young theoretical physicist Pierre Duhem set out his generalised mechanics or "Energetics", a bold design consisting of a unified mathematical framework for physics and chemistry based on the two principles of thermodynamics. He broadened the scope of analytical mechanics, and built up a mathematical theory that spanned from purely mechanical processes to every kind of irreversible transformation, chemical explosions included. He found that at the end of the nineteenth century science was able to describe the complexity of the actual natural world. This theoretical design led Duhem to rediscover and reinterpret the tradition of Aristotle's natural philosophy and Pascal's epistemology. His Energetics could encompass modern science and ancient natural philosophy in a wide and consistent theory. Endowed with a philosophical and historical sensitivity, Duhem went on with clarifying the foundations of science and its history.

# **1** Introduction

Pierre Duhem (Fig. 1) is known and still studied as a philosopher of science and a historian of science: some of his epistemological and historiographical theses, in fact, have long been debated over the twentieth century. He was, however, a theoretical physicist who made important contributions to physics and chemistry.<sup>1</sup> His historical and philosophical research emerged from his scientific practice, and in particular from the need to clarify methods and goals of actual, daily scientific practice.

Duhem found in thermodynamics a unifying theoretical framework for physics and chemistry. At the same time, he recognised in analytical mechanics a very general formal language that could be extended beyond the borders of mechanics. He attempted to build a general theory that would integrate the conceptual basis of thermodynamics with the physical–mathematical apparatus of analytical mechanics. The general theory could also describe irreversible phenomena such as dissipative processes, permanent deformations (hysteresis) and sudden transformations of energy or explosions. To refer to this theoretical enterprise, he used the term *Energetics*, which had already been introduced in 1855 by Scottish engineer William Macquorn Rankine.

A few remarks about the material and intellectual landscape of the late nineteenth century will serve to put into context the process of systematisation of thermodynamics and Duhem's contribution, as well as to introduce us to the theoretical research undertaken by Duhem between 1891 and 1896. Finally, we shall see how this research was followed by acute reflections on the scientific method and original historical reconstructions.

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<sup>&</sup>lt;sup>1</sup> Among the intellectual biographies of Duhem, let us mention [7, 9, 40, 43, 44, 58]. The biography by Jaki is the richest and most detailed, but is rather hagiographic. For an extensive bibliography about Duhem and his collaborators, see [57].

# Pierre Duhem



**Fig. 1** Pierre Duhem [the cover of Pierre Duhem's *Essays in the History and Philosophy of Science* (Hackett Publishing, 1996), where one of the rare photos of the author appears]

## 2 The landscape of the late nineteenth century

Duhem was born in 1861 and lived in France in a time of great changes: the war against Prussia and the German states, the defeat, the bloody uprising of the Commune, the subsequent repression, the collapse of the Second Empire, the birth of the Third Republic and the cultural hegemony of positivism.

In the last decades of the nineteenth century, for the first time in the history of modern science, theoretical advancements led to the spread of technologies that profoundly transformed society. The so-called scientific revolution had changed the intellectual landscape of Europe, but had not led to the material changes longed for by Francis Bacon. In the nineteenth century, chemistry and, subsequently, physics were able to produce real improvements in everyday life. In particular, electrical technologies helped to change cities and homes through the distribution of electricity and the proliferation of telegraph lines [34, pp. 174–80]. The new electrical technologies offered an energy that was clean and easy to transport over long distances. Technologies in general, including those related to thermodynamic machines, played an important role in the emergence of the rhetoric of scientific progress and in the confidence that this progress would promote social progress.

Even before the wide dissemination of new technologies, trust in science decisively influenced the intellectual landscape and gave rise to new currents and philosophical systems. In the six volumes of the *Cours de philosophie positive* that Auguste Comte published between 1830 and 1842, we find a codification of the new scientistic project [13, pp. VII–VIII].<sup>2</sup> Though dominant in many circles, scientistic metaphysics, based on the alleged refusal of metaphysics, was obviously not the only philosophical movement present in the French landscape. We also find the influence of Pascalian epistemology in the debates of the late nineteenth century about determinism and reductionism. We can therefore understand how Duhem found in Pascal an important philosophical reference [32, 60, pp. 2, 5, 9, 13 and 26, 60, pp. 299 and 301].

The professionalisation of physics was achieved in the second half of the nineteenth century. The most interesting phenomenon of this process was the birth of theoretical physics. It emerged from the awareness that the alliance between "meaningful experiences" and "certain proofs", in a Galilean spirit, was not sufficient for the development of a mature scientific practice: it was necessary to build a network of conjectures and models, based on meta-theoretical assumptions that were not always explicitly declared. Between the domain of the empirical practices and the domain of logical and mathematical procedures there was a *theoretical* space which conferred a character of intrinsic historicity and plurality to the whole of scientific practice [11, pp. 83–4; 48, 49, vol. 2, pp. 33, 41–43, 48 and 55–56].<sup>3</sup>

In the second half of the century, electrodynamics and thermodynamics developed as two independent areas with respect to the traditional field of mechanics, considered to be the heart and the paradigm of every good physical theory. Classical thermodynamics, as Rudolf Clausius developed it around the middle of the century, accomplished a theoretical synthesis between the theory of thermal machines of Sadi Carnot and the theory of heat conduction of Joseph Fourier. Clausius introduced the concept of entropy and its cosmological interpretation: the entropy of the universe could not decrease [12, 44, pp. 31–35 and 44]. The concept of entropy was debated and interpreted in various ways, and the general law of increasing entropy in isolated systems was subjected to criticism, especially by British physicists. This new physical quantity proved to be full of consequences in various

<sup>&</sup>lt;sup>2</sup> About the origins and the polysemy of the terms "scientism" and "positivism", see [52, p. 299, note 2].

<sup>&</sup>lt;sup>3</sup> For more about the concept of theoretical physics from the viewpoint of a directly involved physicist, see [2, pp. 5–11] and [4, p. 95].

areas of physics and chemistry and also inspired more general debates, in which scientific content, philosophical reflections and theological debates intertwined [16, p. 123].

The theories of Clausius and Rankine, actually, consisted of two distinct and basically independent parts: a macroscopic theory of thermodynamic transformations and microscopic kinetic models to describe the thermomechanical behaviour of gases. Rankine proposed the first generalisation of the concept of mechanical work, which could be extended to thermal processes or any kind of physical and chemical transformation. The kinetic theory of gases and the microscopic kinetic interpretation of the concept of entropy were later developed by James Clerk Maxwell and Ludwig Boltzmann [7, 56, pp. 210, 213–217 and 222; 1, 47, pp. 43–4, 1, pp. 166–9 and 216–217].<sup>4</sup> The debate about the mechanical-probabilistic interpretation of entropy was very lively and engaged theoretical physicists until almost the end of the century. Henri Poincaré remarked that mechanical models and thermodynamics were inherently incompatible, since the former were based on a principle of reversibility, while thermodynamics included irreversible processes [3, 10, 14, 54, pp. 534–537, 14, p. 246, 3, p. 535, 10, Book 2, p. 622].

Some physicists and engineers proposed a purely macroscopic approach, based on the structural similarity between thermodynamics and the mechanics of potentials and Lagrange equations. In 1869 and in 1876 the French engineer François Massieu was able to derive some thermodynamic quantities and some thermal properties of materials from two thermodynamic potentials [45, 46, p. 859, 46, pp. 2-3, 29, 43]. By the mid-1870s, the American engineer Josiah Willard Gibbs developed the formal analogy between abstract mechanics and thermodynamics, and introduced three thermodynamic potentials, two of which were proportional to Massieu's potentials. In 1882, the influential German physicist and physiologist Hermann von Helmholtz investigated the thermal and mechanical properties of one of Gibbs's potentials, which he called "free energy" [35, 38, pp. 55–6 and 89, 38, pp. 958–9 and 868–869].<sup>5</sup>

# 3 Duhem's general theory

In 1891 Pierre Duhem published a paper in the annals of the École Normale Supérieure, where he had brilliantly earned

a degree and a doctorate.<sup>6</sup> After explicitly acknowledging the contributions of those who had preceded him, especially Massieu, Gibbs, Helmholtz and Oettingen, he put forward a theory based on a set of generalised coordinates among which he included temperature. The theory was developed along two directions. The first involved deriving the mechanical and thermal properties of the system from a potential, according to the scheme already developed by Helmholtz. The second direction aimed at defining generalised thermal capacities, one for each generalised coordinate: one of these, that corresponding to the temperature coordinate, corresponded to the ordinary thermal capacity [17, pp. 234 and 251].

The following year, he published a first article followed by two more with the same title in the *Journal de mathématiques pures et appliquées*. The three papers, all titled "Commentaire aux principes de la thermodynamique", essentially comprised a single essay in three parts. In 1894, in the third part of the "Commentaire", Duhem started from the equations of mechanics and introduced generalised dissipative terms, which were a generalisation of mechanical friction and viscosity. The new terms made a reinterpretation of entropy in abstract mechanical terms possible. The generalisation of the language and notions of mechanics led Duhem to a generalisation of the concept of motion: the motion or displacement in the mechanical sense became a special case of a physical transformation [21, pp. 222–224 and 229].

This outcome was surprising and clearly echoed the Aristotelian language and concept of motion as change and transformation: within the framework of Aristotelian natural philosophy, motion in the modern physical sense was actually a special case of the general concept of motion. The mathematisation of thermodynamics coincided with a generalisation of mechanics, and this generalisation led to an unexpected connection between modern mathematical physics and ancient natural philosophy [21, p. 285].

In that same year and the following one, Duhem published several articles in which he tried to build a mathematical theory for some irreversible processes such as permanent mechanical deformations or hysteresis and subsequently permanent deformations of non-mechanical type, that is, chemical and magnetic hysteresis [22]. Meanwhile, in 1893, he had published a book on chemical processes and in particular electrochemistry, in which theoretical chemistry was based on thermodynamics [19].

In 1896, these different theoretical projects were integrated into a unified theory, in which the search for the general equations of thermodynamics joined the search

<sup>&</sup>lt;sup>4</sup> On the relationship between the kinetic theory of gases and the different atomic models, see [10, book 1, p. 204].

<sup>&</sup>lt;sup>5</sup> For a detailed discussion of this part of the history of physics, see [50, pp. 70, 128–129, 131–132, 147–148 and 155, 42, p. 92, 94–99 and 102, 41, pp. 388 and 394, note 38, 16, pp. 3–4, 15, p. 503 and 505].

<sup>&</sup>lt;sup>6</sup> For biographical information on young Duhem, in particular his attendance of the École Normale Supérieure and the events related to his doctoral thesis, see [9, 40].

for a theory of hysteresis phenomena and the search for a mathematical theory of chemical transformations. The long essay he published shortly after he had moved to Bordeaux to hold the chair of theoretical physics proposed a generalised theory of irreversible and dissipative processes and a mathematical unification of physics and chemistry based on thermodynamics [25]. The term "false chemical equilibria" referred to chemical equilibria that persisted beyond the equilibrium conditions established by the classical theory and that suddenly gave rise to explosive chemical reactions.

The generalised equations of Lagrangian type contained several terms: in addition to the classical terms there appeared dissipative terms that corresponded to the generalisation of static friction and viscosity. The elimination of these terms led to the equations of classical mechanics. The elimination of the traditional kinetic-mechanical or "inertial" terms led to equations that could describe explosive chemical reactions. More precisely, the equations used by Duhem to interpret chemical reactions contained three types of terms: the derivatives of a thermodynamic potential and the two dissipation functions, corresponding to the generalisation of static friction (with its abrupt transition effect) and viscosity. Classical mechanics and chemistry represented the two opposite poles of Duhem's generalised mechanics. Neglecting the generalised dissipative terms led to mechanical processes, while neglecting the inertial terms led to chemical reactions [25, pp. 8, 72-75, 89-91 and 105].

After some simplifications and approximations in the equation for the rate of chemical reactions, Duhem obtained a reaction rate inversely proportional to the generalised viscosity. This meant that, when viscosity vanished, the reaction rate became infinite. From an empirical point of view, this effect was consistent with the presence of an explosive chemical reaction. From a theoretical point of view, it corresponded to a physics in which a finite speed was only guaranteed by the presence of dissipative effects. In the absence of those, speed would become infinite. This physics was structurally similar to the Aristotle's physics, in which bodies move in the presence of a medium. So Duhem was facing a generalised physics and generalised equations of motion, in which excluding some terms led to Newton's and Lagrange's classical physics, while excluding other terms led to a theoretical chemistry that reinterpreted the Aristotelian physics [25, pp. 128–131].<sup>7</sup>

During the years when Duhem had developed his theory, German physicist Georg Helm had proposed a less general *Energetik*, based on the universality of the notion of energy. Helm's *energetist* setting was in turn slightly different from that of another German physicist, Wilhelm Ostwald, which entailed a more accentuated idealisation of the concept of energy and the replacement of the fundamental physical quantity *mass* with energy. Consistently with Rankine's original view, Duhem had developed a wide-reaching mathematical theory, beyond the theoretical horizon of Helm and Ostwald [8, 37, 42, 51, pp. 55 and 65, 51, pp. 159–160, 42, pp. 106–107, 8, p. 223].

#### **4** Reflections on the method

Duhem's physical theory had important consequences for the way of viewing a physical theory and the way in which the history of physics had been passed on. In the same period in which he developed his generalised mechanics, Duhem intensified his reflection on the history and the foundations and methods of science. In 1892 he published his first epistemological article in the Belgian journal Revue des questions scientifiques. Duhem brought to light the complexity of scientific practice, in which the transitions from experience to the preparation of an experiment, from this to the formulation of specific laws and from these to the construction of larger theoretical systems involved a plurality of possible choices. This aspect was also developed in a later article in 1893, where he explored the relationship between physics and metaphysics, which was also open to a plurality of possibilities, in the sense that a physical theory could not in any way imply the adhesion to a specific metaphysical system. The independence of science and metaphysics had to be explicitly stated, although no scientific practice could be said to be completely unaffected by metaphysical influences. In 1894, he clarified the not exclusively empirical character of experimental practice. Its most discussed and criticised meta-theoretical thesis, later described as epistemological holism, asserted that experimental control could not accurately refute a single theoretical statement [18, 20, 23, 31].

In 1894 and in 1896 he also published two historical articles, the first one on the history of optics and the second on the history of the foundations of physical theories during the previous 200 years. He presented a critical history, in the wake of a recent tradition that had been inaugurated by Antoine Augustin Cournot and perfected with extreme philological accuracy by Paul Tannery. In the subsequent years Duhem intensified his research on the history of physics and philosophy of science. The articles he had written between 1892 and 1896 were merged in his book *La théorie physique*. *Son objet et sa structure* [28], which made him famous as a philosopher of science. He presented a re-evaluation of Aristotle's natural philosophy that was far from naïve and regressive [24, 26].

In his more explicitly philosophical texts, Duhem frequently quoted Pascal, who appears to be a fundamental scientific and philosophical reference point. The importance of this influence has been recognised by several scholars, from

<sup>&</sup>lt;sup>7</sup> For a more detailed description of Duhem's general theory, see [7].

the mathematician Émile Picard in 1922, to historians Niall D. Martin and Jean-François Stoffel in the late twentieth century. Pascal had criticised Descartes's mechanism and had stressed the need for a theoretical practice, a synthetic and intuitive one, besides the geometric formalisation. The explicit reference to Pascal increased the intellectual isolation of Duhem, both with respect to the positivist scientism and the neo-Thomist Catholicism. Despite being adverse to each other, both cultural trends agreed with a realistic viewpoint more naïve than Duhem's, who was oriented towards a critical realism, structural in nature rather than ontological. For Duhem, Pascal represented a third way, beyond scientistic dogmatism and philosophical skepticism [44, 53, 59, pp. CXXX and CXXXV–CXXXVII, 44, pp. 68, 90 and 115, 59, pp. 196 and 345].<sup>8</sup>

## 5 The legacy of Duhem

Duhem continued to publish works about generalised mechanics until his untimely death in 1916. In 1903, he published a history of the foundations of physics, in which his theories were interpreted as an attempt to include the complexity of the physical world in the tradition of mathematical physics [27]. In 1911 he published a treatise in two volumes, in which he included a variety of applications to different fields of physics and chemistry [29]. His generalised mechanics did not enjoy great success among physicists and chemists, while it found more attention among mathematicians interested in physics. Chemists found this treatment too formal and mathematised, while physicists were concentrating on the new rays and the exploration of the microscopic processes.

An explicit recognition by scientists who have made original contributions to physics and chemistry came only after World War II. In 1947, Ilya Prigogine emphasised the need to expand the scope of thermodynamics, so as to include irreversible phenomena, states far from equilibrium and open systems. He recognised the role played by Duhem in the construction of a general thermodynamics. In the 1980s, the mathematical physicist and historian of mechanics Clifford A. Truesdell again referred to the unifying power of Duhem's thermodynamics, a theory finally able to clearly describe the real natural processes, that is, irreversible processes. Truesdell saw in Duhem the father of modern rational thermodynamics [55, 61, pp. 1–5 and 95–99, 61, pp. 2, 7, 24–25, 38, 40–41 and 45].

Even though recent theories rely on more sophisticated conceptual and mathematical machinery, Duhem's theory turned out to be structurally fruitful in the long run of history of science.

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<sup>&</sup>lt;sup>8</sup> Bas van Fraassen has highlighted the presence of Pascal's "underground epistemology" in the history of science [33, p. 151]. More recently, Jean François Stoffel underscored the strong influence of Pascal on Duhem, in particular the important role of intuition "next to the certainty of deductive reason" and the search for a third way between scientific dogmatism and skepticism [60, pp. 299 and 301].

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