L&PS – Logic and Philosophy of Science
Vol. IX, No. 1, 2011, pp. 303-313

Duhem's pathway to Thermodynamics

Stefano Bordoni
Department of Foundations of Sciences
University of Urbino – Italy
e-mail: stefano.bordoni-gmail.com

ABSTRACT. Duhem's generalised Thermodynamics was indeed a generalised Mechanics on the track of Lagrange's mathematical physics. From 1886 to 1896 he undertook a demanding design for the unification of physics and chemistry under the two Principles of Thermodynamics. He translated Thermodynamics into the language of Analytical Mechanics, and at the same time he widened the mathematical and conceptual structure of Analytic Mechanics, in order to hold together ordinary mechanics, thermal phenomena, and many kinds of irreversible transformations. In other words, he tried to account for the intrinsic complexity of the natural world. According to Duhem, a sophisticated mathematical physics could replace and widen the scope of the old physics of qualities, arriving at a re-interpretation of Aristotle's natural philosophy. He tried to widen the scope of physics, from "*local motion*" to what he labelled "*motions of modification*".

1. Two Pathways to Thermodynamics

When Duhem undertook his theoretical enterprise, Thermodynamics could rely on a meaningful history. In the 1850s, the Scottish natural philosopher William Thomson tried to integrate the principle of conservation of energy with Carnot's theory of thermal engines. At the same time, Rudolf Clausius put forward the second law of thermodynamics and associated to it a new physical concept, the "*Verwandlungsinhalt*" and then the "*entropy*".[1] Both of them dared a cosmological extrapolation, and Thomson imagined a Universe running towards the thermal death because of the dissipation of energy.

In the 1860s, James Clerk Maxwell made use of statistical concepts in order to obtain the distribution of molecular velocities in a gas. In the 1870s, Ludwig Boltzmann attempted to develop a statistical theory of entropy. The most important novelty was the introduction of probability in physics: probability became an intrinsic feature of physical systems with a huge number of elementary components. Boltzmann tried to go far beyond Maxwell: he was not satisfied with the description of the state of equilibrium. He looked for a law which could also describe the evolution towards the equilibrium.[2]

Boltzmann 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 principle of energy conservation. In Boltzmann's representation, the motion of molecules involved both continuous paths and discrete collisions. Beside the conceptual tension between continuous and discrete representations of physical events, other tensions or dichotomies were at stake: macroscopic versus microscopic representations, reversible versus irreversible behaviour of physical systems, and determinism versus probability.[3]

---

[1] A historical reconstruction of this stage of Thermodynamics can be found, for instance, in Duhem P. 1895, pp. 401-18, and Brush S.G. 1976, Book 2, pp. 568-71. Apart from the time lag between their historical researches, Duhem and Brush put forward different interpretations of the history of thermodynamics, even though they have in common the fact of being both physicists and historians.

[2] 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, 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.

[3] The conceptual tension between determinism and probability has been widely discussed by physicists and philosophers. Cassirer claimed that that tension should not have been interpreted as a contradiction. See Cassirer E. 1936, p. 129. Brush saw a sort of conceptual continuity between the statistical interpretation of thermodynamic irreversibility and the

A different theoretical pathway was undertaken by the Scottish engineer William J.M. Rankine, and by the French engineer Robert Massieu: they put forward a highly abstract, mathematical interpretation of Thermodynamics. Rankine tried to extend the new formal framework to all fields of physics, giving rise to a wide design of unification he labelled "Energetics". Massieu was able to demonstrate that some mechanical and thermal properties of physical and chemical systems could be derived from two potentials or "characteristic functions".[4]

Josiah W. Gibbs and Hermann von Helmholtz developed that abstract re-interpretation of Thermodynamics, and exploited the structural analogy between Mechanics and Thermodynamics.[5]

2. Duhem's General Equations

In 1891, while he was lecturing at Lille University, Duhem published a paper in the official revue of the *Ecole Normale Supérieure,* wherein he displayed what he called the "general equations of Thermodynamics". 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* independent parameters α, β, …, λ. To the Lagrangian parameters α, β, …, λ, and ϑ he associated *n+1* functions R_α, R_β, …, R_λ, R_ϑ which played the role of *generalized thermal capacities*: $dQ = R_\alpha \cdot d\alpha + R_\beta \cdot d\beta + ... + R_\lambda \cdot d\lambda + R_\vartheta \cdot d\vartheta$.[6]

We find a two-fold interpretation of the functions R_α, R_β, …, R_λ, and R_ϑ. According to the mechanical interpretation, they are generalized forces;

indeterminism that emerged from early twenty-century physics. See Brush S.G. 2003, pp. 485-6.

[4] 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. Although mentioned by Josiah W. Gibbs and Duhem, Massieu is almost unknown: the name of "Massieu" does not appear in the *Dictionary of Scientific Biography*.

[5] 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.

[6] Duhem P. 1891, pp. 233-4.

according to the thermal interpretation, they are generalized *thermal* capacities. He reminded the reader that the generalized "*potentiel thermodynamique interne*" $\mathcal{F} = E\left[U - F(\vartheta)S\right]$, where $F(\vartheta)$ was a function of temperature, corresponded to Massieu's "*fonction caractéristique*", Gibbs' "*fonction de force à température constante*", and Maxwell and Helmholtz's "*énergie libre*".[7]

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.[8]

Had something like a *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 the Britih Isles, FitzGerald, J.J. Thomson and Larmor were looking for a new alliance between Lagrangian mechanics and the science of electromagnetic phenomena. On the Continent, a new alliance between Analytical Mechanics and a field theory purified by the concept of force led Hertz to a wide-scope, although very formal, design of geometrization of physics in 1894.[9]

The fact is that in the history of mechanics we must distinguish 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 seat in space or aether. As Hertz remarked in 1892, even intermediate models were at stake in the context of electromagnetic theories.[10]

[7] Duhem P. 1891, pp. 234-5 and 245-7.

[8] Duhem P. 1891, pp. 250-1.

[9] Hertz main aim was the reduction of all physics to an abstract mechanics, wherein "the ideas of force and the other fundamental ideas of mechanics appear stripped of the last remnant of obscurity". See Hertz H. 1894, in Hertz H. 1956, "Author's Preface", p. 1, and p. 41.

[10] Hertz listed four theoretical models: Maxwell's theory corresponded to the fourth model, wherein actions at a distance definitely vanished. See Hertz H. 1892, in Hertz H. 1962, pp. 22-6.

3. A Wide Design of Unification

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: if the latter had tried to give a *microscopic* mechanical explanation of the *macroscopic* laws of Thermodynamics, Duhem assumed those *macroscopic* laws as a starting point. It is worth remarking that, independently from their specific theoretical models, both Boltzmann and Duhem's general attitudes towards Mechanics can be interpreted as a widening of the scope of Mechanics rather than a mere *crisis of mechanics*.

In 1892 Duhem submitted a long paper with the very general title "Commentaires aux principes de la Thermodynamique" to the *Journal de mathématiques pures et appliquées*. It was the first part of a sort of trilogy, whose second and third part were hosted by the journal in 1893 and 1894 respectively. In 1894, in the third part, Duhem made reference to an Aristotelian conception of the word "motion": not only was motion looked upon as a kinematic process, but as transformation in general.

> Nous prenons, dans ce Chapitre, le mot *mouvement* pour désigner non seulement un changement de position dans l'espace, mais encore un changement d'état quelconque, lors même qu'il ne serait accompagné d'aucun déplacement. Ainsi, il y aurait mouvement si les variables que nous avons désignées par *a, b, ..., l* … variaient seules, les variables α, β, …, λ gardant des valeurs fixes. De la sorte, le mot *mouvement* s'oppose non pas au mot *repos*, mais au mot *équilibre*.[11]

At the end of the third Part, Duhem drafted some general "Conclusions", wherein he put his approach to Mechanics and Thermodynamics into a historical perspective. In the recent history of physics, he found two different attitudes towards the relationship between Mechanics and Thermodynamics. On the one hand, most of founding fathers of Thermodynamics had tried to

[11] Duhem P. 1894, p. 222.

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 any "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 second Principle, "Carnot's Principle". In spite of Clausius, Boltzmann and Helmholtz's "daring efforts", the former "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.[12]

4. Duhem's Third Pathway

Duhem saw himself walking on a third pathway: Thermodynamics as a generalized Mechanics, as a wide-scope theory of transformations in a general 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.[13]

His design can be looked upon as a reduction of physics to the language of Analytical Mechanics, but, at the same time, as an anti-reductionist design, wherein the widening of the scope of that language was at stake. In Duhem's

[12] Duhem P. 1894, pp. 284-5.
[13] Duhem P. 1894, p. 285.

"more general science" we can 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".[14]

His mechanism was a sort of *structural* mechanism, which he labelled "Energetics". It was a very general theory similar to Rankine Energetics: it was a generalised Mechanics as well as a generalised Thermodynamics. We find a remarkable conceptual distance between Duhem and some upholders of *energetics* like Helm and Ostwald. They insisted on the principle of the conservation of energy as the sole foundation of physics. In particular, Ostwald developed a physical world-view wherein "the concept of matter, which has become indefinite and contradictory, had to be replaced by the concept of energy".[15] In no way can the name of Duhem be associated to this kind of *energetism*.

REFERENCES

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

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

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

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. 2003, "Irreversibility and Indeterminism: Fourier to Heisenberg", in Brush S.G. 2003, (Hall S..N. ed.) *The Kinetic Theory of Gases*, Imperial College Press, London, pp. 480-504.

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.

[14] Duhem P. 1894, p. 285.
[15] See Ostwald W. 1896, pp. 159-60.

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

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

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

Duhem P. 1895, *Les théories de la chaleur*, in Duhem 1992, pp. 351-441.

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.

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.

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 dagerstellt)*, Barth, Leipzig; English translation in Hertz H. 1956, *The Principles of Mechanics*, Dover, New York.

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

Ostwald W. 1896, "Zur Energetik", *Annalen der Physik und Chemie* 58, pp. 154-67.

Rankine W.J.M. 1855, "Outlines of the Science of Energetics", in Rankine W.J.M. 1881, pp. 209-28.
Rankine W.J.M. 1881, *Miscellaneous Scientific Papers*, Charles Griffin and Company, London.