

Chapter 10

On Duhem's Energetics or General Thermodynamics

Abstract Pierre Duhem is an unavoidable figure if one wants to scrutinize the progress in the mixed science of mechanics and thermodynamics in the period 1880–1920. He is a prolific writer and a never tired propagandist of the global science of energetics. Here we examine his main contribution, its novelty and its inherent limitations in the light of two remarkable synthetic and/or critical works, his treatise on energetics (*Traité d'énergétique ou de thermodynamique générale*. Gauthier-Villars, Paris, 528+504 pages, 1911) and his series of papers (Duhem in *L'évolution de la mécanique*. A. Joanin, Paris, 1903) on the “Evolution of Mechanics” (of which we also provide a partial translation). These works are replaced in their socio-scientific background with its main sources (Gibbs and Helmholtz) and its possible interaction with, and influence on, contemporary scientists. A particular emphasis is put on Duhem's style and interests that are strongly influenced by his combined epistemological, philosophical and historical vision. We concentrate on the specialized fields examined and tentatively improved by Duhem in the “Evolution of mechanics”, with a personal interest in those “nonsensical branches”—friction, false equilibria, permanent alterations, hysteresis—that Duhem tries to attach to the former Gibbs' statics and Helmholtz' dynamics by way of subtle generalizations. In this analysis we account for the enlightening comments of contemporaries (E. Picard, J. Hadamard, O. Manville), of his various biographs, and of Duhem's own perusal (Duhem in *Notice sur les titres et travaux de Pierre Duhem*, 1913) of his oeuvre. We conclude with modern developments which provide answers to queries of Duhem that now appear as too much in advance on their time.

10.1 Introduction

Pierre Duhem (1861–1916), probably one of the most powerful intellects of his period, is a remarkable character. He combines in one person a brilliant and sharp mind, a prolific writer and contributor to phenomenological physics, the champion

of energetics, a philosopher of science, and the true creator of the history of medieval science. To delineate somewhat the scientific landscape of the relevant period—to fix ideas, 1880–1920—we note that his great contemporaries are, among others, Josiah W. Gibbs (1839–1903), Herrmann von Helmholtz (1821–1894), Henri Poincaré (1854–1912), Ernst Mach (1838–1916) [46], Jacques Hadamard (1865–1963), Henrik A. Lorentz (1853–1928), Albert Einstein (1879–1955), Max Planck (1858–1947), James C. Maxwell (1831–1879) and Lord Kelvin (1824–1907) in the UK, and Joseph V. Boussinesq (1842–1929) in France. Gibbs and Helmholtz are his heroes (cf. [52]). Poincaré and Hadamard are mathematician friends; Mach is a fellow traveller on the road to energetism. Lorentz and Planck are “atomists” and partisans of particles and of molecules (the worst that can be for Duhem). Einstein is beyond the understanding of Duhem (and of many others at the time—but this is not a valid excuse). As to Maxwell (his “bête noire”), Kelvin and Boussinesq, although Duhem had to recognize their creativity, they rely too much on the notion of (mechanical) models to be considered serious and exemplary “theoretical” physicists. In all his works Duhem avoids the use of words such as “particles” and “molecules”, hence his a priori rejection of Lorentz and Planck. This agrees with Duhem’s profound dislike for hidden motions of hypothetical masses.

Duhem is one of the most prolific authors in his period of activity (roughly 1880–1915); he published twenty-two books in forty-five separate volumes, as well as nearly 400 articles and book reviews in scientific and philosophical journals [56]. He corresponded with about 500 correspondents in all scientifically active countries during his life. His outstanding production can be divided in three large fields: phenomenological physics (elasticity, acoustics, electromagnetism, and physical chemistry—which he usually calls “theoretical physics” and would probably be better designated nowadays as “mathematical physics” because of its definitely marked style), epistemology and philosophy of science, and history of science (with an emphasis on old cosmology—view and explanation of the world—and the sciences of the Middle Ages). Practically, no actual scientist can peruse the whole of this multi-faceted production, because we do not—and cannot—have the vast knowledge and cultural education of these late nineteenth-century scientists.

For the curious reader, we mention that several biographies of Duhem have been written, some hagiographic, some more reasonably scholarly but also biased by some religious and philosophical vision: e.g. Ariew [2], Brouzeng [9], Humbert [39], Jaki [40] and Pierre-Duhem [59]. But to know him better from the scientific viewpoint which is our main concern, we shall mostly refer to the eulogy by Picard [58] and the thorough review of Duhem’s work on physics by Manville [47]. Picard was a pure mathematician but with a good understanding of Duhem’s works. Manville was a direct disciple of Duhem in Bordeaux; he is sometimes much clearer than Duhem himself. To this we must add Hadamard’s [36] kind appraisal of Duhem’s contributions to mathematics.

10.2 On Duhem's Style and General View of Science

Here, we can only focus on some aspects of his works on phenomenological physics although one cannot avoid acknowledging the inevitable interrelations between his physics and his epistemological views (his religious opinions and political views, strongly as they may have been expressed and so much influential on his life and vision of the world, are to be left out). Even such a limited perusal is difficult for several reasons: an obvious one is that science and more particularly physics was not written in Duhem's time as they are written now. A second reason is that Duhem, in particular, writes in a very literary (sometimes verbose) style, making extremely long sentences and involving much repetition. He makes an abusive use of semi-colons (as shown in the texts that we translated in the Appendices; Note that this was in the fashion of the time if you consider with sympathy Proust's style). This makes it difficult to follow some of the expanded arguments.

But above all, Duhem, being a pioneer in the field he develops, introduces new words and expressions that have not necessarily passed in our own scientific vocabulary. In what follows, we have to face expressions used in a nonconventional manner such as "mechanics" (when he means a phenomenological theory involving in some sense the notion of "motion"), "doctrines" (where he means types of approach, or simply theories), "motion" (by which he means not only classical local motion but also alterations such as during the fusion of ice, or phase transformations), "velocities" (sometimes meaning reaction rates), and "false equilibria" (that are his own invention). "Gibbs' or Helmholtz' mechanics" does not necessarily refer to mechanics in our accepted sense. Thus some interpretation is necessary. Many of his statements would have been much better expressed with few mathematical symbols. But it happens that Duhem's physics was ahead of the mathematics that would have been best fitting. Duhem was a classical analyst, by what we mean someone trained essentially for dealing with standard ordinary and partial differential equations. He was missing our present knowledge (that is still by force limited) in differential geometry, functional analysis, dynamical systems, and convex analysis. Many of the questions he raised and the horizons he opened would find an answer and a broadening in these fields of mathematics, as amply proved by successful developments in the rational mechanics of continua in the second part of the twentieth century (see [54, 66, 67]).

In the philosophy and methodology of science Duhem wrote two remarkable books, one on the *Aim and Structure of Physical Theory* (original French—Duhem [25, 26]) and the other with a title repeating Plato's motto "*To save the phenomena*" (original French—Duhem [27]—with Greek title). In the first of these he exposes at length the under determination of theory by fact, the rejection of metaphysics and models (as used by, e.g., Kelvin and Maxwell in the UK and Boussinesq in France), and natural classification, rather than explanation, as the very object of physical theory (this can be discussed); according to Duhem, "a physical theory is not an explanation; it is a system of mathematical propositions

which has for aim to represent, as simply, completely and exactly as possible an example of experimental laws”.

The contents of the second book are clearly explained by its title. Science is elaborated so as to “save the appearance” of actually occurring phenomena; its formulas should not contradict experience. This is the only good criterion of truth. This vision is close to true pragmatism and is not so far from Poincaré's conventionalism. Metaphysics is foreign to pure science. All this had a definite influence on Duhem's own science, the development of which he sees with a high degree of continuity, and as a collective enterprise. This last point justifies his constant use of the plural (collective and not “royal”) “we” and not the personal “I”, referring [29] appropriately to a citation from Blaise Pascal's *Pensées*.¹

About pragmatism, we should ponder the words of Miller [56]: “While for other doctrines a new truth is a discovery, for the pragmatic scientist, it is an invention”.²

For our main concern in this contribution, the most relevant writing of Duhem is the one on the “evolution of mechanics” [24]. In one chapter of this opus, Duhem examined what, at the time, he called the “*nonsensical*” *branches of mechanics*. What he means by this somewhat eccentric expression are the fields of physics, mechanics and electromagnetism that do not fit yet in his general framework of thermodynamics. It is interesting to note the list of these fields to which we shall return in Sect. 10.4: so-called false equilibria, friction, hysteresis phenomena, and electro-magnetic theory in materials. These are precisely dissipative phenomena such as thermodynamically irreversible reactions, plasticity, visco-elasticity, memory effects, etc. Now looked upon with our present knowledge, this sounds like a tentative proposal of research programme for the next generation, something quite equivalent in its own field to the Erlangen program (1872) of Felix Klein in geometry and the list (1900–1902) of unsolved—at the time—problems proposed by David Hilbert in pure mathematics—that in fact included the axiomatization of the whole of physics—in particular, Mechanics—as

¹ In the original French: «Certains auteurs, parlant de leur Ouvrages, disent: mon livre, mon commentaire, mon histoire, etc.... Ils sentent leurs bourgeois qui ont pignon sur rue, et toujours un «chez moi» à la bouche. Ils feraient mieux de dire: notre livre, notre commentaire, notre histoire, vu que d'ordinaire il y a plus en cela du bien d'autrui que du leur». In translation: “Certain authors, in speaking of their works, say: my book, my commentary, my history, etc. They smack of these bourgeois homeowners, with “my house” always on their lips. They should rather speak of: our book, our commentary, our history, etc., since, generally speaking, there is far more in them of others than of their own” (cf. [29], in translation).

² It is interesting to ponder the confusion between “discovery” and “invention”. Usually, “discovery” refers to finding (un-covering) something that pre-existed (e.g., the laws of physics) while “invention” refers to something entirely new (essentially in technology). But in French law the person who “discovers” by chance a treasury (say a box full of old gold coins) is legally called the “inventor” (and not the “discoverer”) of this treasure! But the “un-covering” relates to something that was hidden. Think of the first view of the hidden face of the moon, once the human kind could go around the moon. Of course, the so-called hidden face existed before! Was it “discovered” or “invented”? This is a conundrum that we propose to the reader.

Problem no. six. We shall focus on this specific point, providing the reader with partial English translations of the above referred to text and of the introduction to his magisterial treatise on energetics (cf. Appendices A and B).

10.3 Some of Duhem's Creative Works in Thermo-mechanics

Nowadays Duhem is still the subject of many studies in epistemology and philosophy of science in spite of his neglect or belittling by well known historians and philosophers of science such as Clagett [11], Koiré [43], Bachelard [3–5] (and his “epistemological fracture”), and Kuhn [44] (and his “paradigm shift”)—all more or less partisans of a “discontinuous” evolution of science. In contrast, his hard science is seldom explicitly discussed, either because its main interest was not captured or because it is implicitly accepted and therefore no longer referred to in detail. Duhem is mostly recognized as one of the creators of *physical chemistry* (with Gibbs) and a forceful contributor to *energetics*, placing the works of William J. Macquorne Rankine (1820–1872) [61], Rudolph Clausius (1822–1888), Hermann von Helmholtz (1821–1894), Ernst Mach (1838–1916) [46], and Wilhelm Ostwald (1853–1932) at the top of his list of favourite sources and/or competitors. Duhem's view on the unifying role of energetics or general thermodynamics in all of physical sciences (mechanics, electricity and magnetism, heat, etc.) is masterly but quite lengthily expanded in his treatise on “energetics” or “general thermodynamics” [28] which he wrote as some kind of definite treatise. This, as we shall see, has a strong flavour of axiomatic nature that will influence Clifford A. Truesdell and his followers in the 1950s–1960s.

10.3.1 *Physical Chemistry*

Duhem is undoubtedly one of the creators of physical chemistry and thermochemistry together with Gibbs, van t'Hoff, Ostwald, and Arrhenius. Gibbs and Duhem corresponded; Duhem [16] wrote the first critical analysis of the Gibbsian theory [34] of equilibrium of heterogeneous substances, and one of Duhem's doctoral students came from the USA to pursue the Gibbs-Duhem line, a sufficiently rare fact at the time to deserve being underlined. This culminated in the labelling of a fundamental law for solutions as the *Gibbs-Duhem equation*. Following Helmholtz and F. J. D. Massieu (1832–1896)—an altogether too much neglected scientist (but see Massieu's fundamental work of 1869 [48])—Duhem makes a systematic use of the notion of potential—or characteristic function—where (according to [56, p 229]) “others were still using osmotic pressure as a measure of chemical affinity and using artificial cycle to prove theorems”.

One of Duhem's fruitful ideas was to consider reactions rates as (generalized) velocities; this yielded the notion of thermodynamic variables having no inertia, hence governed by first-order differential equations in time, and in the end resulting in forces proportional to the "velocity", a much Aristotelian sounding concept in the view of many. Inspired by the rational mechanics of John Bernoulli, d'Alembert and Lagrange, he could then apply the general notion of virtual variations and virtual work not only in physics but also in chemistry. This also led Duhem to use the expression "motion" for so many evolving situations and that of "mechanics" for many physical alterations. It is in this sense that one must interpret Duhem's general expressions such as "Gibbs' mechanics" [i.e., "chemical mechanics"] and "Helmholtz' mechanics" (see the frequent use of these expressions in Appendices A and B below). But the appropriate introduction of potentials allowed Duhem—by analogy with rational mechanics—to envisage the importance of the problem of maxima and minima in the study of the stability of chemical equilibria. In his typical generalization and application of concepts in various branches of knowledge Duhem did not hesitate to introduce this notion of stability in epistemology while commenting on problems of instability studied by Hadamard.

Duhem was generous in the diffusion of his views in physical chemistry. His first opus on the subject [15] is an epoch making one—although he was still an assistant at the *ENS* in Paris. He also wrote a short introductory course [19], "elementary" lessons for chemists [23], and a so-called "elementary" treatise of chemical mechanics, based on thermodynamics (in four volumes, Duhem [21]) for a total of more than 1,400 pages and dealing with all aspects of the subject (including the continuity of liquid and gaseous states, the dissociation of perfect gases, vaporization, homogeneous solutions, dissolutions, two-component mixtures, and heterogeneous systems).

10.3.2 Fluid Mechanics, Viscous Fluids

Usually Pierre Duhem is not remembered as a contributor to fluid mechanics. But this vision is erroneous. As a matter of fact, he was instrumental in developing some critical points (cf. First volume of Duhem [17]). Among these we note: (1) in the case of nonviscous fluids, problems of hydrodynamic stability with the first application of general theorems going further than Lyapunov and Hadamard, and the problems of buoyancy with much improvement over the former analysis of Bouguer, Euler, and Abbé Bossut; here also Duhem applies the notion of virtual displacement to the problem of the stability of floating bodies going further than the analysis by Lagrange and Lejeune-Dirichlet; (2) in the case of viscous fluids, Duhem paid special attention to the possible propagation of waves. Some time before, Christoffel and Hugoniot had given a precise definition to the notion of waves. J. Hadamard [35] perfected the approach by defining (the order of) a wave front in terms of the quantities that are continuous—so-called invariants across the

front—or discontinuous across them. For perfect compressible fluids this yields the two longitudinal and transverse waves. But Duhem, a passionate of thermodynamics, clearly specifies the various possible conditions whether the fluid is heat conductor (velocity according to Newton) or not (in which case it is Laplace's formula that applies). This he extended to discontinuity waves of any order (in the classification of Hadamard).

But the main discovery of Duhem in this field is that no true discontinuity wave can propagate in a viscous fluid; shock waves in the sense of Riemann cannot exist. Accordingly, what we can observe in air (a slightly viscous fluid) are not true discontinuity waves with vanishing thickness across which the derivatives of the velocity would vary abruptly, but are in fact extremely thin layers, that Duhem calls “quasi-waves” (nowadays we say “*structured shock waves*”) across which the velocity varies very rapidly although continuously. E. Jouguet (1871–1943), a direct disciple of Duhem, then showed that an almost sudden increase of entropy takes place through this layer. All this input in the theory of fluid mechanics is well abstracted by Duhem [29] himself in his notice written a few years before his untimely death. He also introduced the notion of what we now call contact discontinuities.

Finally, it is generally forgotten that it is Duhem who proved the celebrated inequalities to be satisfied by the viscosity coefficients λ and μ of Navier-Stokes equations ($3\lambda + 2\mu \geq 0$, $\mu \geq 0$) the same year as Stokes, from the non-negativity of the corresponding dissipation.

10.3.3 Deformable Solids

Duhem is probably better known in solid mechanics than in fluid mechanics. A reason for this may be the direct influence he had on some well known contemporaries such as Poincaré and the Cosserat brothers [13] (see also Hellinger [38]), and the fact that he was much interested in large deformations, the study of which had a tremendous development some 50 years later on.

When Duhem reports his investigations in elasticity he is aware of, and praises, the main works by George Green, G. Kirchhoff, W. Thomson (Lords Kelvin), W. Voigt (considering isothermal and adiabatic deformations), and J. V. Boussinesq on elements of nonlinear elasticity; the Cosserat brothers have formulated a rigorous theory (1896), and Hadamard has applied it to obtain a beautiful theorem—Duhem's words [29, p. 100]—concerning wave propagation. Thus Duhem “kept alive a correct finite elasticity inspired by other workers” [56]. In the course of these works, Duhem was the first to study the relationships between waves in isothermal and adiabatic finitely deformed systems without viscosity. Again, the specific interest of Duhem in thermodynamic properties led him to establish conditions of stability and those of the existence of waves (in the sense of Hadamard): no true shock waves can exit in the viscous non-linear thermo-elastic bodies (a result already shown in viscous fluids; see above). In these studies he is

also led to introducing the notion of “ondes-cloisons” [“partition (-wall) waves”, GAM] through which there is no exchange of matter. These waves are similar to contact discontinuities (no discontinuity in the velocity). They separate the volume of the considered body into cells, so that Duhem notes their resemblance with H. Bénard's cells in a fluid where large differences in temperature generate convection currents and the formation of cells. All this is well documented in notes published in the *Ann. Ecole Normale Supérieure* between 1904 and 1906, but also in the collection of papers gathered in his book on “*Researches in elasticity*” (Duhem [25, 26]; fourth part on waves in viscous and non-viscous media), while his first works in elasticity are presented in the second volume of Duhem [17] which reproduces courses he delivered early in his career in Lille.

Solids in plastic deformation are dissipative with possible permanent alterations and hysteresis. This will be briefly examined in [Sect. 10.4](#) below.

10.3.4 General “Thermo-mechanics” and Thermodynamic Potentials

The general attitude of Pierre Duhem towards what we now call «thermo-mechanics»—emphasizing thus the intimate relationship between thermodynamics and the rational mechanics of continua—is the extensive use of the notion of *potential*.

First among his contribution was his complementary study of Gibbs' relation that is now known as the *Gibbs-Duhem equation*: this thermodynamic relationship expresses changes in the chemical potential of a substance (or mixture of substances in a multi-component system) in terms of changes in the temperature θ and the pressure p of the system. The *chemical potential* μ represents the Gibbs' free energy per molecule of the substance; the change in μ is the amount of energy per molecule available to do work for a process such as in a chemical reaction at constant temperature and pressure. The celebrated Gibbs-Duhem equation reads thus:

$$N d\mu = -S d\theta + V dp,$$

where N is the number of molecules of the substance, S is the entropy of the system, and V is the volume. This equation follows from a combined application of the first and second laws of thermodynamics. In practice, it means that if the chemical potential is known for each substance under one set of conditions, then this equation can be integrated to find the corresponding chemical potential under a different set of conditions. A modern application would be the evaluation of the amount of energy that a car battery can deliver. The relationship is thus of universal application if we account for the rich variety of useful chemical reactions.

The other applications of the notion of potential are more subtle. First, following Helmholtz, and also Massieu [48], Duhem recognized the importance of

the notion of *characteristic function*, or potential. Also in the path of Helmholtz, Duhem enforced the notion of *normal variables of state*, according to which entropy is given a special status among the list of independent variables appearing in the relevant potential (nowadays, the internal energy) [this distinction is of importance if we remember that the dual of entropy is none other than the thermodynamic temperature, obviously a very original quantity].

Among the other notions of potential considered by Duhem, we must single out those of “*internal thermodynamic potential*” (equivalent to the potential in rational mechanics), “available energy” (useful energy according to Kelvin and equal to the *free energy* of Helmholtz), “ballistic energy” (cf. [29, p. 87]) (practically equivalent to the modern notion of total potential energy) with the related problem of minimization, and that of “*oeuvre*” (in fact, total energy). Duhem is one of the first to define heat in terms of energy and work [both Caratheodory, and also Born [6] will follow along this line].

Concerning thermo-mechanical variables, Duhem introduced the notion of *variables exhibiting no inertia*, and thus to be governed by differential equations of the first order in time. In Duhem's own words, chemical “mechanics” is the typical domain of application of this concept. Although this smells of some Aristotelian mechanics (“force” proportional to the “velocity”—i.e., rate of change), this will have a glorious descent with the modern notion of *internal variable of state* (See Sect. 10.5 below). Anyhow, most of these notions, with some unavoidable evolution in the employed vocabulary, permeate the whole of modern continuum thermo-mechanics (cf. [53]).

10.3.5 Contributions to Mathematics

This is just to complement the preceding paragraphs. Hadamard, a friend of Duhem, wrote a very kind and obviously benevolent appraisal of Duhem's contributions to mathematics (cf. [36]). Of course, he does not claim that Duhem is a creative mathematician because Duhem did not create new mathematical concepts, and his mathematics is that of the field of differential and integral calculus (i.e., standard analysis); but Duhem was aware of the recent developments in the field, in particular concerning problems of maxima and minima, e.g., a certain familiarity with Lyapunov's studies.

What is most characteristic of Duhem is his *mathematical style*, in a line that will yield the formulation of mathematical physics in the twentieth century, and provide inspiration to some members of the community of rational continuum physics (including the present writer in his youth). Hadamard, but also Picard [58], emphasizes the rigour given by Duhem to theorems in elasticity, thermo-elasticity, and general theorems for Navier-Stokes fluids and the finite elasticity in (Kelvin-Kirchhoff-Neumann) bodies. As noticed by Miller [56], “No wonder that Duhem's contemporaries often remarked that many of his papers opened with the barest of assumptions followed by a series of theorems, with little motivation for the proposed

“axioms” and hardly any appeal to experiment”. This style was going to influence a whole school mainly in the USA (cf. [54], Chap. 5, and Sect. 10.5 below). On a more trivial level, it is relevant to note that Duhem was the first good exploiter of Euler's theorem on homogeneous functions in physics. This also will prove useful later on, especially in the thermo-mechanics of elasto-plasticity (cf. [50]).

10.4 Short Analysis of Some Exemplary Writings

For the purpose of illustration and test of our understanding of Duhem's style of writing, we consider in greater detail two of his works for which we provide partial translations into English (Appendices A and B) [Some comments are directly inserted in the text of the English translation, within square brackets].

10.4.1 *On the General Treatise on Energetics*

First, as an unavoidable obligation, we consider the introduction to Duhem's formidable treatise on energetics of 1911 (Appendix A below). It is no question to envisage a full translation of the whole treatise (a seldom read opus in any case) that would provide a rather dull and boring reading to most modern readers who, anyway, do not have the keys to decipher the code of Duhem's specific vocabulary. As we see it, this introduction defines clearly the aim of the treatise by shedding light on its main purpose. It recalls the objective followed by what Duhem calls “theoretical physics” [this is *not* our current assumption of the term]: *From given physical data, extract new physical laws*. It emphasizes the prevailing role played by *general principles*, for instance, the principle of conservation of energy and the principle of Carnot [a primitive form of the second law for heat machines]. Duhem reminds the reader that *Rational Mechanics* was for a long time the basic “code” for the general principles of physics. But he wants to account, not only for changes in the local motion of objects and in their geometrical form [this was the subject matter of rational mechanics], but also for changes in other “*qualities*” or *states* exhibited by material bodies. This includes thermal, chemical and electromagnetic ones, indeed all what is now the object of phenomenological physics.

The ideal frame for such a global vision is provided by *energetics* (in the sense of Macquorne Rankine who provided an outline of this general framework Rankine [61, 62]) or, in other words, *general thermodynamics* [a term clearly preferred by Duhem] since all physical effects, whatever, must comply with the two basic laws of thermodynamics. Later on, the local form of the second law will be called the *Clausius-Duhem inequality* by Truesdell and his followers, putting thus Duhem on an equal footing with Clausius, the true creator of the second law.

Then Duhem, following his philosophical and epistemological inclination, cannot avoid specifying his views on the relationship between theory and experiments: “theoretical physics” remains free of choosing its own path (see Duhem’s [25, 26] “Aim and Structure of Physical Theory”), the relevant principles remaining themselves without logical support, but nonetheless with a historical one.

The reader will find in Capecchi [10, Sect. 18.1] a brief but deeply thought analysis of the contents of the first part (first “tome”, devoted to non-dissipative systems) of Duhem’s treatise. This we shall not repeat, noting simply that Capecchi attempts to define what Duhem understands by the rather unclear notion of “oeuvre” (in this author’s translation, “activity”): essentially a generalization of mechanical work.

10.4.2 *On the Evolution of Mechanics*

The second work of Duhem that deserves a closer examination is his series of papers on the *Evolution of Mechanics* because, on the one hand, it is normally written for the layman [we would rather say the enlightened amateur], and on the other hand, it poses queries that will have to be answered in the future. This series of papers was an immediate success with early translations into Polish and German [but the first English translation had to wait for more than seventy years, thus showing the distance between British physics and Duhem’s one]. We provide in Appendix B our own English translation of essential parts of Chapter VII of this opus. The whole of this series provides pleasant and informative reading but with the charm of an old-fashioned style.

In Chapter I Duhem presents the various kinds of mechanical explanations with the identification of Aristotelian, Cartesian, Newtonian, and Leibnizian viewpoints. Chapter II is devoted to analytical mechanics with due consideration of virtual velocities, d’Alembert, Lagrange, Poisson, Boscovich, Navier, Cauchy, and Gauss. Chapter III is devoted to the mechanical theories of heat and electricity including the essential contributions of Clausius, Helmholtz, Boltzmann and Gibbs for the theory of heat, and of Faraday, Maxwell and Helmholtz for electromagnetism. We have dealt with Duhem’s preference of Helmholtz’ approach over that of Maxwell in Maugin [52]—also [Chap. 7](#) in this book. Chapter IV deals with atomism and what Duhem calls the return to Cartesianism. In this line he cites William Thomson (Kelvin), Maxwell, Heinrich Hertz, Boltzmann, and Bousinesq, a line for which he shows no great sympathy (cf. his harsh criticism of the use of mechanical models). In contrast, he sketches the foundations of thermodynamics in Chapter V, rendering full justice to Macquorne Rankine. Here he emphasizes the fact that “*it is possible to speak about physical quantities in the language of algebra*” (p. 301). It is here that he introduces the notion on *virtual variation* (“modification”) applied to all kinds of physical quantities, as also the general notion of *alteration* (e.g. change of state) generalizing thus the notions of “motion” and “equilibrium” to non-mechanical concepts. The conservation of

energy and the relationship between work and quantity of heat are underlined. “Reversible” modifications are then considered and the limitations brought by the Carnot principle (positive sign of the external work during a cycle) complete this magisterial vision.

Chapter VI on general «statics» and «dynamics» is central in that it defines what Duhem usually calls “Gibbs’ mechanics” and “Helmholtz’ mechanics”. It is badly needed to understand the more thought-provoking last chapter. Advocating the consideration of normal variables of state because the latter provide the simplest formulation of thermodynamics, Duhem rightly emphasizes the role of the characteristic function of Massieu. This is—in varied naming—the “available energy” for Gibbs and Maxwell, the “free energy” for Helmholtz, and the “internal thermodynamic potential” for Duhem. From this quantity one can deduce the necessary and sufficient conditions for a system to remain in equilibrium under the action of external bodies maintained at the *same* temperature as this system. Accordingly, the mathematical form of this assertion is obtained by considering a virtual modification that does not change the temperature. This is in the spirit of Lagrange’s variations. With F denoting the free energy and A the external action, this equilibrium condition for a normal variable α typically reads

$$A = \frac{\partial F}{\partial \alpha}. \quad (10.1)$$

Both spirit and methods of Lagrange’s statics have been transferred to this Gibbsian formulation, including, if necessary, the introduction of side conditions (mathematical constraints). Its fertility is most obvious in the study of qualitative properties such as in electricity and magnetism. Its greatest success, however, was in the theory of chemical mixtures with the proposal of the *rule of phases* by Gibbs himself. With Eq. (10.1), thermodynamics acquires a large extension, much beyond the mechanical aspects envisaged by Lagrange. In particular, it allows one to determine calorific properties. This follows from the fact that once we know the internal potential of a system, then we can compute its internal energy. Furthermore, an infinitesimally small reversible modification is none other than a virtual modification issued from an equilibrium state. The heat produced in this operation can be determined from the internal potential, and divided by temperature, it (Clausius) provides the associated decrease in entropy (i.e., $\delta S = \delta Q/\theta$).

Equation (10.1) will be completed by an “acceleration term” J_α if the state variable α is endowed with an appreciable inertia and the system is in “motion” [meaning in general by this an “evolution in time”]. This “dynamics” would be obtained by applying *d’Alembert’s principle*. But there may also exist viscous phenomena which make that, in the absence of inertia, return to equilibrium is delayed [This is akin to relaxation]. These viscous effects will always result in a non-negative working in any real evolution. This is locally written as $-v_\alpha \delta \alpha \geq 0$ with the sign convention of Duhem for v_α . With both inertia and viscosity—represented by a term v_α —Eq. (10.1) is replaced by

$$A + J_\alpha + v_\alpha = \frac{\partial F}{\partial \alpha}, \quad (10.2)$$

remembering that this is strictly valid only for a constant temperature. This is Duhem's elaboration of "Helmholtz' mechanics" with further works in Krakow in Poland by Władysław Natanson (1864–1937; see [63]) in the period 1896 on. In Eq. (10.2), we must reckon that J_α will involve second-order time derivatives, while the "viscous" contribution v_α will depend, not only on temperature, but also on the generalized velocity associated with variable α . The problem of initial conditions is therefore posed. The latter reduces to knowing only the initial state if the normal variable α has negligible inertia. Such variables are extremely important in many chemical systems or systems exhibiting material changes (e.g., phase transformations).

But the information contained in the above exposed principles and equations is insufficient to solve the whole dynamical problem at hand. The needed additional relations are based on the computation and sign of the produced heat and resulting entropy change. This is nothing but the celebrated *Clausius inequality* that will later be known as the *Clausius-Duhem inequality*. To end with this chapter, it is natural, as done by Duhem, to ask what is the relationship of (10.2) with the equation governing the *kinetic energy* (the "living force" in the old vocabulary)? We can think of multiplying all terms in (10.2) by an infinitesimal change in α , i.e., $\delta\alpha$. This will yield

$$-\delta K_\alpha + A\delta\alpha + v_\alpha\delta\alpha = \frac{\partial F}{\partial \alpha} \delta\alpha, \quad (10.3)$$

remembering that K_α is the kinetic energy associated with α , $-\delta K_\alpha$ is the decrease in kinetic energy, and the partial derivative of F was computed at *constant* temperature so that the right-hand side of (10.3) is not the full variation of F . It is this remark that made Duhem introduce the notion of useful energy. Indeed, we can rewrite (10.3) as

$$\delta K_\alpha - A\delta\alpha = -\delta F - S\delta\theta + v_\alpha\delta\alpha, \quad (10.4a)$$

or

$$\delta K_\alpha - A\delta\alpha = -\delta E + \theta\delta S + v_\alpha\delta\alpha, \quad (10.4b)$$

with

$$S = -\frac{\partial F}{\partial \theta}, \quad E = F + S\theta. \quad (10.5)$$

The first of these is the definition of *entropy*, while the second introduces the *internal energy*. Duhem calls the left hand side of (10.4a) or (10.4b) the variation of useful (available) energy U . We see that U is none other than F for isothermal evolutions ($\delta\theta = 0$), and none other than E for isentropic evolutions ($\delta S = 0$),

both in the absence of viscous effects. If we remember that $-v_x \delta \alpha \geq 0$, then we also see that (10.4a, b) yields³

$$-v_x \delta \alpha = A \delta \alpha - \delta(K_x + F) - S \delta \theta \geq 0 \quad (10.6a)$$

or

$$-v_x \delta \alpha = A \delta \alpha - \delta(K_x + E) + \theta \delta S \geq 0. \quad (10.6b)$$

The notion of useful energy receives its whole importance in discussions relating to the stability of an equilibrium state where isothermal and isentropic stabilities are quite different. According to Duhem, it is a postulate due to Helmholtz ("the heat capacity is positive in all systems") that resolves the matter.

10.4.3 On Permanent Alterations and Hysteresis

Now we can have a closer look at Chapter VII of Duhem's "Evolution of Mechanics" for which we give a partial English translation in Appendix B below. This offers a direct continuation and generalization of the contents of Chapter VI. This chapter is quite ahead of its time and introduces queries than could not find an answer in the early twentieth century. But, altogether, we can say that Duhem is on the right track by underlining some branches of mathematical physics which, at the time, appear more or less as nonsensical ("aberrantes"), i.e., not yet fully absorbed in the general science of energetics. We shall concentrate on four kinds of phenomena: friction, false equilibria, permanent alterations, and hysteresis phenomena, leaving aside the case of electromagnetism to which we have contributed many research works and several books certainly in a perspective that Duhem would have appreciated [33, 49, 55] since entirely based on a thermo-mechanical vision.

The phenomena of interest are precisely *dissipative* ones such as thermodynamically irreversible reactions, plasticity, visco-elasticity, and memory effects. The first section of this chapter concerns friction and chemical false equilibria. If

³ In modern continuum thermo-mechanics, a transcription of these two equations for a whole body B reads (cf. [50], p. 39, Eqs. 2.54 and 2.55):

$$\Phi_{\text{intr}} = P_{\text{ext}} - \frac{d}{dt} \int_B \left[\frac{1}{2} \rho \mathbf{v}^2 + F(\cdot, \theta_0) \right] dv \geq 0 \quad (\text{Na})$$

and

$$\Phi_{\text{intr}} = P_{\text{ext}} - \frac{d}{dt} \int_B \left[\frac{1}{2} \rho \mathbf{v}^2 + F(\cdot, S_0) \right] dv \geq 0 \quad (\text{Nb})$$

for isothermal and isentropic transformations, respectively. Here Φ_{intr} is the total intrinsic dissipation and P_{ext} is the power expanded by external forces.

friction is an easily comprehended phenomenon, the phenomenon of *false equilibria*—an expression coined by Duhem—is difficult to grasp; perhaps that they should better be called *quasi-stable equilibria*. In order to introduce this notion, Duhem first clearly defines the notion of reversible changes and then, by way of examples, the theory of mixtures and friction, he develops the notion of *false equilibrium* (see below) for which a new “mechanics” (he means *thermo-mechanics*) is needed. For this one must go farther than Gibbs and Helmholtz who exploited the notion of potential. This will ultimately yield the idea of *irreversible* changes. This irreversibility is defined by negation of reversibility. Miller [56, p. 228] says that Duhem gave “the first precise definition of a reversible process; earlier versions by others (unfortunately often preserved in today’s textbooks) are too vague”... “The reversible process between two thermodynamic states A and B of a system is an unrealizable limiting process. The limit of the set of real processes for getting from A to B is obtained by letting the imbalance of forces between the system and the surroundings at each step tend toward zero. Each member of this set of real processes must pass through non-equilibrium states, or else nothing would happen”. Duhem also emphasizes the relative appraisal of what is a state of equilibrium. We now return to his original text, p. 418.

To illustrate his discussion, Duhem considers a thermodynamic system with only one *normal* variable of state, say α . We remind the reader that the notion of *normal* variable of state was introduced by Duhem following an idea of Helmholtz: a system of normal variables of state χ_α in the functional dependence of internal energy density E does not include entropy η which, serving to define temperature, is considered as a very special variable, i.e., $E = E(\eta, \chi_\alpha)$; in terms of the free energy, this endows the thermodynamic temperature with a special status and we shall write $F = F(\theta, \chi_\alpha)$. The action of friction—to which we are naturally accustomed—is always positive (with the sign convention of Duhem) and “will depend, just like the action of viscosity, on the absolute temperature, the variable α , and the generalized velocity $\dot{\alpha} = d\alpha/dt$ ”. However, contrary to what happens for viscosity, “it will also depend on the external action A ”. Also, “it will not vanish with the generalized velocity; the latter going to zero, the action of friction will tend to a positive value g ”. The additional term to be added to Eq. (10.2) above—written for α —will have a sign that depends on the sign of the generalized velocity. We can summarize Eqs. (10.3) and (10.4b) of Duhem in the single equation:

$$A + J + v - \text{sign}(\dot{\alpha})f = \frac{\partial F}{\partial \alpha}. \quad (10.7)$$

With the same working hypotheses, the corresponding equilibrium condition “will no longer be represented by an equality, but by a double inequality that expresses that the absolute value of the difference $A - \partial F/\partial \alpha$ is not larger than g ”, i.e., [Eq. (5) in Duhem]

$$\left| A - \frac{\partial F}{\partial \alpha} \right| \leq g. \quad (10.8)$$

Here Duhem says only a few words on the equation of living forces [equation of kinetic energy], noting that “it is only necessary to add the work of friction to the work of viscosity. The former, like the latter, is always negative. We also do not deal with the Clausius-inequality which remains exact in the new dynamics. Here also, the work of friction is just being added to the work of viscosity. Other consequences of the laws just formulated, and more particularly the condition of equilibrium, will require a little more attention.

Now, Gibbs' statics, as recalled above, “would require the difference $A - \partial F / \partial \alpha$ to vanish, and therefore having [this is a truism] value between $-g$ and $+g$. The equilibrium states predicted by this Statics, and that are usually called states of *true equilibrium*, are thus among those that are predicted by the new Statics; But the latter announces the existence of an infinity of other equilibrium states, that we designate by the name of *false equilibria*”. Citing Duhem in our translation: “If the value of g is large, then the states of false equilibrium spread on both sides of those of true equilibrium, in a large domain. They will shrink close to the states of true equilibrium whenever the value of g is small. If this value becomes sufficiently small, then the states of false equilibrium will be so close to those of true equilibrium that experiments would no longer distinguish them; practically, the Statics of systems with friction would be undistinguishable from Gibbs' statics”. We can say with Duhem that “Gibbs' Statics and Helmholtz' Dynamics are limit forms of the Statics and Dynamics of systems with friction; these tend to those when the action of friction becomes infinitesimally small”. This remark is not a simple view of the mind; it acquires a particular interest in the study of chemical equilibria. This will be exploited by E. Jouguet in his theory of explosions. But Duhem also tries to illustrate his notion of false equilibrium by some mechanical example, such as the possibility, when considering the problem of the possible rolling of a small ball down a rough hill, that in addition to the true equilibrium at the top of the hill, the small ball may stop for short instants along the rough slope. But in the rest of this section Duhem expands a better example from chemical physics. Miller [56, p. 230] rightly comments that “real false equilibria can also be considered as instances of extremely slow reaction rates”. This seems to be the viewpoint adopted nowadays.

Section II of this chapter rings a more familiar bell to our ears, for it deals with *permanent “alterations” and hysteresis effects* that may be closer to our own plasticity, visco-plasticity and creep concepts. Here Duhem first gives a general idea of what permanent alterations are. He emphasizes the role of infinitesimally slow evolutions, adapting in accordance temperature and external actions. Again, one must go beyond Gibbs' statics and Helmholtz' dynamics. That is, one must elaborate on the generalization of Eq. (10.2) or its incremental form that seems to be more appropriate. More precisely, Duhem discusses the possible generalization of the following incremental form that follows from equilibrium [Eq. (10.1)]

$$dA = d \frac{\partial F}{\partial \alpha}. \quad (10.9)$$

Here we remind the reader that $\partial F/\partial\alpha$ is computed at constant temperature while noting that systems exhibiting permanent alterations (e.g., residual strains) are quite different from those exhibiting viscosity [but in modern thermo-mechanics we also envisage a mix of the two effects as visco-plasticity]. The permanent alterations envisaged by Duhem are exhibited when an unloading (decrease in the “cause”) following a loading, does not bring the system back to its initial virgin state. We must thus distinguish between the two possibilities of the incremental law that will generalize (10.9) depending on whether we are increasing or decreasing the “cause”. For sufficiently slow evolutions, Duhem proposes to generalize (10.9) by [cf. Duhem’s Equations (7) and (7b)]

$$dA = d\frac{\partial F}{\partial\alpha} + h \operatorname{sign}(d\alpha)|d\alpha|, \quad (10.10)$$

where the quantity h may still depend on the state of the system and also on the external action A . Equation (10.10) may seem to be both enigmatic and ad hoc to most readers. It is however in direct line with mathematical works on hysteresis of the 1970s–1990s (see [7, 51]). To find more elaboration by Duhem on (10.10) and applications one should consult the original works of Duhem published in 1901 in a rather odd place (Belgium). Here Duhem is satisfied with the cases of deformations, residual magnetization, magnetic hysteresis, and analogous properties for electric polarisation in dielectrics. Duhem emphasizes the interest of his considerations in metallurgical treatments (tempering, annealing, etc.). But much more is also to be found in the exhaustive and clear analysis of Manville [47]. The latter author remarks that it is difficult to summarize the works of Duhem and his co-workers (doctoral students: Marchis, Saurel, Pélabon, Lenoble) on permanent alterations and the somewhat 400 pages of various memoirs (in particular the seven published in Belgium in 1896, 1897 and 1901) in a short text [20, 22]. But some of the facts and properties recalled by Manville shed light on some aspects that will be of great interest for further comparison with modern developments.

First, for an isothermal infinitesimal transformation we can rewrite (10.10) as

$$dA = \frac{\partial^2 F}{\partial\alpha^2} d\alpha + \bar{h}|d\alpha|. \quad (10.11)$$

For an ever increasing value of α , $d\alpha = |d\alpha|$, and (10.1) yields the differential equation

$$\frac{dA}{d\alpha} = \frac{\partial^2 F}{\partial\alpha^2} + \bar{h}(\alpha, A, \theta), \quad (10.12)$$

which defines a family of ascending curves in the plane (A, α) . By the same reasoning, with ever decreasing value of α , we will define a family of descending lines; This vision allows one to build closed cycles and to define a line of “natural states”. We note that for an infinitesimal modification that causes the passing of a state (α_0, A_0, θ) to a state (α_1, A_1, θ) (10.11) also yields

$$A_1 - A_0 = \frac{\partial^2 F}{\partial \alpha^2} (\alpha_1 - \alpha_0) + \bar{h} \sum |d\alpha|. \quad (10.13)$$

If the external action recovers its initial value, then $A_1 = A_0$, and (10.13) yields the "permanent" alteration

$$(\alpha_1 - \alpha_0) = - \frac{\bar{h}(\alpha, A, \theta)}{(\partial^2 F / \partial \alpha^2)} \sum |d\alpha|. \quad (10.14)$$

The condition

$$\bar{h}(\alpha, A, \theta) = 0 \quad (10.15)$$

defines the *line of natural states* in the plane (A, α) for a given temperature.

The second important remark is that from the law of displacement of the equilibrium (a *stability* condition about an equilibrium: cause and effect vary in the same sense), the perturbing work in passing from (A, α) to $(A + dA, \alpha + d\alpha)$ must be non negative (Eq. (9), p. 310, in Manville [47])

$$dA.d\alpha \geq 0. \quad (10.16)$$

This has for immediate consequence that the slopes of the curves in the (A, α) plane must always be in the same sign whether on increasing or decreasing A . Consequently, the end points of a hysteresis cycle in the plane (A, α) are always sharp and cannot be rounded.

A third remark concerns the extension of Clausius' theorem for a non-reversible closed cycle. The quantity

$$\int dS = \int \frac{dQ}{\theta}$$

over a cycle ought to be non-negative. With constant temperature, this reduces to the condition

$$\int dQ \geq 0.$$

Equivalence between heat and work yields that $dQ = A d\alpha$ for an isothermal cycle, and thus

$$\int_{\text{closed cycle}} A.d\alpha \geq 0. \quad (10.17)$$

This clearly dictates the sense in which hysteresis cycles are necessarily followed in the plane (A, α) .

In practice it was soon discovered that many hysteresis cycles (especially in the mechanics of deformations) are slightly rounded at their ends. The explanation of this phenomenon in contradiction with (10.16) is to be found in the likely presence of small viscous effects. Duhem had several graduate students working out the

experimental facets of this research on permanent alterations (Theses of Marchis⁴ and Pélabon in 1898, and of Saurel and Lenoble in 1900; see in particular [45]). Results were not very conclusive from the quantitative point of view. Only a general qualitative agreement was found (cf. [47, p. 350]). Sophisticated experimental techniques and accurate measurement possibilities were not yet available at the time, so that these studies were probably too ambitious and in some sense doomed. Here are Duhem's own words: "It seems that no theory of permanent alterations can obtain from experiments more than qualitative and somewhat vague confirmations" (as cited by [47, p. 599]).

In page 423 of his "Evolution of mechanics" Duhem in fact goes more deeply in the notion of natural state and that of residual fields, and then he discusses the possible dynamics—we admit hard to apprehend—in which the standard application of d'Alembert's principle is at fault, referring to works by Henri Bouasse (1866–1958; a French physicist in Toulouse, South-west of France) and the noted German physicist Max Wien (1866–1938).

In the long Section III, pp. 424–427, Duhem considers the general thermodynamics of electromagnetic bodies. He ponders the notions of electromagnetic energy, electric displacement, electromagnetic induction, electrodynamic forces, properties of the system which have no inertia associated with the relevant variables, in spite of the existence of generalized velocities duly associated with such variables, electrodynamic potential, electrokinetic energy, and Ohm's effect considered as a viscosity. He pays an emphatic tribute to Helmholtz. He clearly expresses his irreconcilable appraisal of Maxwell's vision. This, of course, appears to be outdated and certainly not very objective.

The long conclusion (pp. 427–429) of this study is typical of the style of Duhem and of his talent. He provides a rather literary synthesis of the contents of the whole work. He does not hesitate to compare the construction of his successive theories—his *New "Mechanics"*—to the "sanguine sketches" of Raphael that are on exhibit at the Louvre museum. There you can examine at leisure the formidable advances of the work of Raphael by successive approximations "starting from a rough sketch and then improving the details at each successive stage and finally producing a masterpiece that finally causes the admiration of all" (p. 428). This may be a bit exaggerated when applied to one's own work. But Duhem is certainly right in defending his progressive complexification of the approach by including more and more "nonsensical" branches that badly require some formalisation and a sound thermodynamic basis. Indeed, the physical world is complex, and its

⁴ Lucien Marchis (1863–1941), interested in all means of transformation of energy and transportation, became a professor at the University of Paris in 1910 when a chair financed by the (armament) magnate Basil Zaharoff was created especially for him at the Sorbonne. This was endowed with a substantial amount of money that allowed the collection of a formidable roster of books on aerostation (balloons, Zeppelins) and the beginning of aviation from all over the world. This chair was transformed into a Chair of Aviation and then a Chair of Aerodynamics after the Second World War. Our Institute inherited this formidable collection of which we became the curators.

phenomenological approach cannot be over simplified—in particular mathematically—even though its very nature ignores the notions of particles and molecules. In agreement with Duhem's epistemological vision, the construction of this New Mechanics goes further than Gibbs and Helmholtz but it is still guided by Lagrange and d'Alembert on a rational, mostly mathematical, path. This is the credo of Duhem at a time that is not so ready to accept it. Examining its immediate reception and its delayed legacy is our next endeavour.

10.5 Influence on Contemporaries and Later on

Duhem's original works are seldom directly cited in the beginning of this twenty-first century, i.e. about one century after these works. Indeed, we must realize the extraordinary rapid evolution of his main fields of concern, continuum mechanics in the large and electromagnetism, in this lapse of time. We have surveyed this progress in a recent book [54]. But much of this progress has been made possible thanks to his critical thinking, his embryonic studies, and his deepest works. His own contemporaries followed and applied his works and he did much to advertise and popularise them through his many writings and his huge correspondence with fellow scientists from the world over. The sheer bulk output of his numerous works was of course efficient for this, but the resonance of his works with many interests of the time was also a determining factor. The only obstacle to this swarming of ideas may have been his aerial view, much above the head of many of the less universal thinkers among his contemporaries, and also his personal style, with its inherent complexity and sometimes obscurity already highlighted in [Sect. 10.2](#).

In dealing with this influence we must distinguish between the direct reception by contemporaries, the acceptance and exploitation of seminal ideas, the deepening of the ideas of irreversible thermodynamics, and the renascence of some of Duhem's ideas in the emergence of a true thermo-mechanics with its successful application to the so-called “non-sensical” branches of mechanics.

In the period 1890–1920 the most cited works of Duhem are those on elasticity, waves and physical chemistry. Like for Poincaré, the writing of lecture notes is the occasion for Duhem to revisit the corresponding scientific matter and to introduce new developments. This is particularly the case of his early book (*Hydrodynamique, élasticité, acoustique*, 1891 [17]). The revisited results and proofs given in this opus are often cited by Poincaré, the Cosserat brothers [13], Appell [1] and Hellinger [38]. The most original part deals with finite strains and, later on, the application of Hadamard's classification of discontinuity waves [35] to elasticity and thermo-elasticity. This will have a glorious descent with works by Truesdell [64] and those gathered in Coleman et al. [12]. Another work of influence was the one devoted to stability and the notions of available and ballistic free energy. This was taken over by Ericksen [31, 32, p. 9].

Physical chemistry, the domain of excellence of Duhem, obviously received most attention. In this line, combining this very field and arguments of wave

propagation, E. Jouguet (1871–1943) is probably the most successful direct disciple of Duhem—see in particular Jouguet [41, 42]. Complementing the Rankine-Riemann-Hugoniot theory of shock waves, Jouguet has created the theory of *detonation waves* with application to high explosives. Here the now well known Chapman-Jouguet condition states that the detonation propagates at a velocity at which the reacting gases just reach the sound velocity (in the frame of the leading shock wave) as the reaction ceases. Chapman and Jouguet (circa 1900) in fact stated this condition for an infinitesimally thin detonation front (remember there is no more a true discontinuity front). The physics of this process will be improved by Zel'dovich (USSR), von Neumann (USA) and Döring (Germany) during the Second World War, giving rise to the so-called ZND model.

As to seminal ideas, they are of different magnitude and sometimes relevant more to hearsay than anything else. The idea of *normal* variables of state was readily incorporated in thermo-statics (Caratheodory, Born). The idea of *internal variables of state* to be fully exploited in the 1970–1990s is, according to Truesdell [65, p. 39], to be found in Duhem [28], although we think that Bridgman [8] was more articulate and more successful, in particular with his own influence on the thinking of J. Kestin. It is also said that it is Duhem [18] who may be responsible for the idea to enrich the kinematics of continua by adding to each material point a set of “directors” (unit vectors) in order to provide internal degrees of rotation, an idea that will be fully developed by the Cosserat brothers in their very original book of 1909 [14] (this book introduces the notion of what are now called *Cosserat media*). According to Edelen [30, p. 44], the notion of *non-local continua*—another path to generalized continuum mechanics where the dependence of stress and body force at a point on the state of the *whole* body must be considered—may also be traced back to this decidedly imaginative work of Duhem [18]. Finally, we must record that Duhem was instrumental in fruitfully exploiting the notion of homogeneous functions in thermodynamics (more on this to follow below).

The flame of Duhem’s approach to general thermodynamics was successfully carried over by Th. De Donder (1872–1957) and other physicists from the Netherlands and Belgium between 1930 and 1970, resulting in the now commonly admitted *theory of irreversible processes* (S. de Groot, P. Mazur, I. Prigogine)—for short *T.I.P* [60]. However, both Duhem and these scientists did not possess the mathematical tools—such as convex analysis and nonlinear optimization—to deal with some of the properties (plasticity, hysteresis), so that they could deal only with *linear* irreversible processes. The solution would come in the 1970s–1980s for *nonlinear* irreversible processes (see below). We simply note that in *T.I.P* the residual non-negative dissipation is obtained as a bilinear expression in “forces” and “generalized velocities”. The closure hypothesis is a linear expression of one of these in terms of the other with signs respecting the second law, hence the *linear* qualification certainly most often valid for a very small departure from thermodynamic equilibrium (for which the axiom of local thermodynamic state holds good). This makes the dissipation quadratic, i.e. homogeneous of degree *two* in the velocities (think of Rayleigh’s dissipation potential). But some of the “nonsensical” effects are of a different nature, often involving the notion of threshold or

maximum critical load, and with the strange property of a dissipative effect not depending on the speed at which the cause is applied. Typically, this is what happens in the plastic response of materials not sensitive to the strain rate: “plastic deformation appears to be a process of energy dissipation but at constant state” (Bridgman). As a consequence, the corresponding dissipation is a homogenous function of degree *one* only (in the velocity), obviously a case not manageable by Duhem and standard *T.I.P.*

Now we can examine how Duhem's “nonsensical branches of mechanics” received a satisfactory thermodynamically admissible framework by abandoning some of the working hypotheses of—but deviating the least from—*T.I.P.*, but in fact corroborating some of Duhem's mathematical proposals in Chapter VII of his “*Evolution of Mechanics*”. Plasticity, visco-plasticity, creep, damage, phase transformations, magnetic and electric hystereses are among these phenomena that attracted most of the attention of mechanicians of materials and applied mathematicians in the last forty years. The thermodynamic answer to the paradoxical situation created by plastic like behaviours was to be found in the consideration of thermodynamics with *internal variables* of state and properties of *convexity* applied to both the internal energy and a pseudo potential of dissipation. Note that the word “convexity” practically never appears in Duhem's writings. But this is an essential notion that appropriately replaces a usual notion such as quadraticity. The *non-linear* thermodynamics of deformable bodies is based on this notion.

As to internal variables of state (Bridgman, Kestin, Gurtin and Coleman), they are identifiable representative parameters of the resulting macroscopically irreversible process. Although being measurable by a gifted experimentalist, they are not directly controllable by external actions, and they obviously are not equipped with an inertia (remember Duhem's variables without inertia). They evolve only under the influence of an evolution of the observable variables, e.g. the local state of stress. Without elaborating further this field of thermo-mechanics (see details in [53]), it suffices to notice that some basic re-interpretation of thermodynamics is necessary, in particular an axiom of *local accompanying state* (Kestin) has to replace the axiom of *local state* of classical thermodynamics. The short but remarkable note by Moreau [57] was essential in introducing the required mathematical notion of convexity, and consequently variational inequalities. Then the French school (Germain, Mandel, and their students; also Ziegler [68] in Switzerland) was instrumental in establishing the corresponding formalism. Of particular efficiency was the model presented by Halphen and Nguyen [37] of so-called “generalized standard materials”. Denoting by α the set of relevant internal variables—this denomination cannot be due to pure chance—it was then possible on the basis of convexity arguments and the existence of a pseudo-dissipation function of appropriate degree of homogeneity to prove some of the mathematical results of Duhem, e.g., Eqs. (10.16) and (10.17) above. For example, with the anelastic (plastic) infinitesimal strain ε_{ij}^p considered as an internal variable of state (a reasonable hypothesis), equations similar to (10.16) and (10.17) are *proved* in the form

$$\dot{\sigma}_{ij}\dot{\epsilon}_{ij} \geq 0, \quad (10.18)$$

and

$$\int_{\text{closed strain cycle}} \sigma_{ij} d\epsilon_{ij} \geq 0. \quad (10.19)$$

The first of these is known as the local stability condition of Drucker and the second as Ilyushin's postulate in the community of plasticity, but now they are proved on a thermodynamic basis. More on this and the cases of magnetic and electric hysteresis is to be found in Maugin [50, 51, 53]. This constitutes a true neo-Duhemian approach.⁵

It appears thus that with appropriate notions of convexity and homogeneity, the proposed programme of Duhem concerning his “nonsensical branches” of mechanics could be fulfilled. The unanswered question here is whether Duhem's writing was very much influential in these developments. We must avoid here the temptation of “precursoritis”; we must admit that we do not know for sure if the thinking of people like J. Kestin—who read French and was the most knowledgeable specialist of all types of thermodynamics—J. Mandel and others was directly influenced by Duhem or by one of his disciples. For instance, Jouguet was a professor of mechanics at both *Polytechnique* and the school mines in Paris when Mandel was a student in these two schools. Jouguet who had a marked interest in the historical development of mechanics and thermodynamics, must have more than simply mentioned the works of his mentor, so that there might have been more continuity than we originally thought.

In retrospective, we must recognize that Duhem's work in physical chemistry “provided a whole generation of French physicists and chemists with their knowledge of chemical thermodynamics” [56, p. 228]. But Miller also wrote [56, p. 232] that “by mid [twentieth] century Duhem's scientific work had been almost completely forgotten”. As to the famous “nonsensical branches”, he says that “as of this writing [56, p. 229] there is no really adequate thermodynamic theory of such systems, although interest in this subject has recently been revived”. We hope to have sufficiently documented the spot on recent developments herein and in various works to disapprove Miller's mild appraisal.

⁵ *Personal touch.* In (at the time, 1975) secrete document (report on my French Doctoral Thesis in Mathematics), a well known French mathematician (great geometer also interested in the history of physics), André Lichnerowicz, classified my approach to the thermo-mechanics of relativistic continua as *neo-Duhemian*—but I had not yet read Duhem in those times. When I could read this document after a law was passed giving access to all such personal matters, I felt that this was intended to be derogatory by its author (I may be misinterpreting), who could not figure out how much I later became pleased with such a classification.

10.6 Conclusion

Duhem may have been, with Poincaré, Bouasse and some others, the last scientists to tackle all branches of phenomenological physics simultaneously. This may even be truer of Duhem than of his colleagues because of his all embracing energetic vision. These are bygone days. Furthermore, no doubt that Maxwell's theory of electromagnetism on the one hand and the triumph of atomic theories on the other have put shades on some of his work and diminished the relative importance of his contributions in some fields of science. However, the main purpose of the present contribution was not to exhibit the belated success of his vision—although this is not to be neglected—but to show how his work contributed in a timely and critical manner to the development of phenomenological physics at a turning moment of its history, between the mathematical works of the nineteenth century “giants” (Green, Cauchy, Kelvin, Kirchhoff, Helmholtz, Stokes, Maxwell, Saint-Venant, Boussinesq and Voigt), the consolidation of true engineering sciences (for which Duhem shows no specific interest), the return to experimental bases and molecular considerations, and the emergence of quantum and relativistic physics. The wealth and significance of Duhem's works remain astonishing to our eyes if we accept to have a benevolent look. Surprisingly enough, as shown in the preceding section, some of his most discussed and misunderstood works seem now to be in resonance with fruitful recent developments. This of course teaches a lesson: the full success of a mathematical theory of nature occurs only with the simultaneous availability of ad hoc mathematical tools, the conception of appropriate experimental devices and, now, the exploitation of successful numerical techniques. Unfortunately, the original work on energetics by Duhem could not comply yet with the last three requirements. In contrast, the present theory of the “mechanics of materials” does, although certainly inspired by Duhem's premature achievements.

Appendix A

Partial English Translation of P. Duhem, “*Traité d'énergétique ou thermodynamique générale*”, Gauthier-Villars, Paris, 1911, by Gérard A. Maugin [Only the Introduction and small parts of Chapter I: “*Définitions préliminaires*”, are translated in order to give a flavour of Duhem's style and exposition. Original footnotes, if any, are reported to the end and numbered consecutively. Translator's remarks are placed within square brackets in the main text. This is a verbatim translation without any ambition of literary prowess.

Traité d'énergétique ou thermodynamique générale

Treatise of energetics or general thermodynamics

By Pierre DUHEM

Introduction

1. Of thermodynamics or energetics

Theoretical physics represents by means of quantities (*grandeurs*) the properties of the bodies that it studies. Methods of measurement allow one to place in correspondence, with a more or less broad approximation, each intensity of a property with a particular determination of the quantity that represents this property. Through the methods of measurement, each physical phenomenon corresponds to a set of numbers, each physical law corresponds to one or several algebraic relations between various quantities, each set of concrete bodies to a system of quantities, to an abstract and mathematical scheme.

Theoretical physics has constantly to solve the following problem: *From given physical data, extract new physical laws*; either it proposes to show that the latter, already directly known, are none other than consequences of the former, or it proposes to announce laws that the experimentalist has not yet observed.

To treat this problem theoretical physics combines given laws together, that concern particularly certain physical properties and certain bodies, in agreement with rules issued from *general principles* that are supposed to hold true for all properties and all bodies.

For example, it wants to show that if we know the law of pressure of the saturated vapour of a liquid, and the laws of compressibility and dilatation of a liquid and its vapour, then one can fix the law according to which the heat of vaporisation varies; to this purpose, it combines the first laws along the rules of the *principle of conservation of energy* and the *principle of Carnot*, principles that are supposed to apply to all bodies and all of their properties.

It is the system of these general principles that we propose to expose here.

For a long time, physicists have assumed that all properties of bodies reduced, in the last analysis, to combinations of figures [geometrical forms] and local motions. The general principles to which all physical properties must obey, were none other than the principles that govern the local motions, i.e., the principles that compose *rational mechanics*. Rational mechanics was the code for the general principles of physics.

The reduction of all physical properties to combinations of figures and motion or, following commonly used denomination, the mechanical explanation of the Universe, seems today to be condemned. It is not so for a priori reasons, whether metaphysical or mathematical. It is condemned because it has been so far just a project, a dream, and not a reality. Despite immense efforts, physicists never succeeded to conceive an arrangement of figures and of local motions that, treated following the rules of rational mechanics, give a satisfactory representation of a somewhat extended set of physical laws.

Is the attempt at a reduction of all physics to rational mechanics, an always vain attempt in the past, destined to succeed one day? Only a prophet could answer this question positively or negatively. Without prejudging the meaning of this answer, it appears wiser, provisionally, to renounce their efforts, fruitless until now, towards the mechanical explanation of the Universe.

Therefore, we are going to attempt at a formulation of the corpus of general laws to which all properties must obey, without assuming a priori that these properties are all reducible to a geometrical figure and a local motion. Accordingly, the corpus of these general laws will no longer reduce to rational mechanics.

In truth, the geometrical figure and the local motion remain physical properties; they are in fact those that are the most immediately accessible. Our corpus of general laws must apply to these properties, and, being applied to the latter, it must recover the rules that govern the local motion, the rules of rational mechanics. The latter must, therefore, result from the corpus of general laws that we propose to constitute; it must be what follows when we apply these general laws to particular systems where we account only for the figure of bodies and their local motion.

The code of the general laws of physics is known nowadays under two names: the name of *thermodynamics* and the name of *energetics*.

The name of *thermodynamics* is intimately attached to the history of this science; its two main principles, the principle of Carnot and the principle of conservation of energy, were discovered when studying the motive power in machines exploiting fire. This name is also justified by the fact that the two notions of work and quantity of heat are constantly at play in the reasoning through which this theory develops.

The name of *energetics* is due to Rankine¹; the idea of *energy* being the first that this theory has to define, the one to which most other used notions are attached; this name seems to us as well chosen as that of *thermodynamics*.

Without deciding which naming is preferable to the other, we shall use both as equivalent to one another.

2. On the logical significance of the principles of energetics

The logical character of the principles that we are going to formulate and group together must be borne in mind².

These principles are pure *postulates*; we can state them as we please, on the condition that the statement of each of them is not self contradictory, and that the statements of the various principles are not in reciprocal contradiction.

The character with which we recognize that the *whole set* of the so formulated principles constitute a good theoretical physics is the following one: applying this set of principles to formulas that represent exact experimental laws, we can deduce new formulas which, in turn, represent other exact experimental laws.

The experimental control of the set of principles of energetics is thus the only criterion of truth of this theory.

Indeed, this control can be done only on the whole set of principles of energetics taken in its totality or, for the least, on extended parts of this set. It would be impossible to submit to the control of experiment one isolated among these principles, or even a small number of these principles. Any experiment, simple as it may be, involves in its interpretation very many and diverse principles. We will often have the opportunity to recognize this fact in the course of this exposition.

The experimental control can only concern the whole set of ultimate consequences of the theory; it estimates if this set of consequences provides, or does not

provide, a satisfactory representation of these experimental data; but in so far as the theory has not produced the set of these last consequences, we cannot call for this control, as this would be premature; hence the following rule which will be of frequent usage in the sequel of our studies: *In the course of it exposition*, a theoretical physics is free to choose the path that it likes, in so far as it avoids any logical contradiction; in particular, it does not need to account for any experimental fact; it is only when it has reached the end of its development that its ultimate consequences can and must be compared to experimental laws.

To say that the principles of energetics are pure postulates and that no logical constraint limits our right to choose them arbitrarily, is not to say that we will formulate them by chance. On the contrary, we shall be very strictly guided in the choice of these statements, knowing well that it would suffice to alter any thing for the experimental check of the consequences to become at fault at some point.

We are assured by this guideline by our knowledge of the past of science. Principles have been formulated that were proved to be in gross contradiction with experiment; other principles were then substituted to them, which have received a partial confirmation, although an imperfect one; then they were modified, corrected, guaranteeing for each change a more exact agreement of their corollaries with facts. We are assured that the clothing of which we cut the forms will fit exactly the body it must dress because the blueprint has been tried and retouched many times.

Each of the principles that we shall state presents thus no logical proof; but it would carry a historical justification; we could, before stating it, enumerate the principles of differing forms that were tried before it, and which could not fit exactly reality, that we have been forced to reject or to correct until the whole system of energetics adapts in a satisfactory manner to the set of physical laws. The fear of an excessive length will forbid us the exposition of this historical justification.

Notes by Duhem

1. J. Macquorne Rankine, *Outlines of the science of energetics* (Glasgow Philosophical Society Proceedings, Vol. III, no.6, 2 May 1855). – J. Macquorne Rankine, *Miscellaneous scientific papers*, p. 209.
2. We will limit ourselves to giving here a very concise résumé of what we expanded in the following book: *La théorie physique, son objet et sa structure*, Paris, 1906 [English translation: *The aim and structure of physical theory*, Princeton University Press, New Jersey, 1954; paperback reprint, 1991]. This work can be viewed as a kind of logical introduction to the present treatise.

Appendix B

Partial English Translation of P. Duhem, "L'évolution de la mécanique – Part VII – Les branches aberrantes de la thermodynamique", *Revue générale des sciences*, pp. 416-429, Paris, 1903, by Gérard A. Maugin [Only small parts of this lengthy contribution are translated; Original footnotes, if any, are reported to the end and numbered consecutively. Translator's remarks are placed within square brackets in the main text. This is a verbatim translation without any ambition of literary prowess.

Duhem P. (1903), *L'évolution de la mécanique* (published in seven parts in: *Revue générale des sciences*, Paris; as a book, A. Joanin, Paris) [There exists already an English translation: *The evolution of mechanics*, Sijthoff and Noordhoff, 1980, to which we had no access].

L'évolution de la Mécanique

The Evolution of Mechanics

VII- The nonsensical branches of thermodynamics

I.- Friction and chemical false equilibria

From the original text, p. 418:

That outside systems of which the equilibrium states can always be classified in reversible changes, there exists an infinity of other systems of which the statics is not that of Gibbs, and the dynamics not that of Helmholtz, and that, among such systems, are precisely those exhibiting friction?

Therefore, the laws according to which systems with friction evolve or remain in equilibrium, require a specific formulation. This formulation, we will not ask it to chance. The formulation imposed to statics by Gibbs and to dynamics by Helmholtz was shown to be admirably fruitful; it is natural to conserve its type as much as possible; to deduce the new formulation from the old one by means of additions and modifications as light as possible; this is the idea that guided us when we built the mechanics of systems with friction.

It would not be easy to expose the latter with entering details that the present writing should not involve. However, let us try to draw a summary sketch and, to that purpose, we restrict ourselves to the study of a system such that only one normal variable, apart from temperature, suffices for its definition. Let α represent this unique variable. If F , A , J , v are, respectively, the internal potential [energy], the external action, the inertial force, and the action of viscosity, then according to Helmholtz' dynamics at each instant we can write the equality

$$A + J + v = \frac{\partial F}{\partial \alpha}. \quad (3)$$

This equality, the general law of motion [probably "evolution" would be better] of the system, implies the law of its equilibria, a law in conformity with Gibbs' statics.

The equilibrium of systems with friction does not agree with Gibbs' statics; Equality (3) does not apply to them; but we can try to modify it in such a way that it will be extended to such systems.

To that purpose, we continue to attach to each state of the system a quantity F that is determined without ambiguity through the knowledge of this state. To this quantity that we still call internal potential, we will continue to attach internal energy and entropy by means of previously known relations; the external action, the inertial force and the action of viscosity will remain defined just as before; but these elements will no longer be sufficient to set forth the equation governing the system. It will be necessary to know a new element, the action of friction f .

This action, always positive, will depend, just like the action of viscosity, on the absolute temperature, the variable α and the general velocity $\dot{\alpha} = d\alpha/dt$; but contrary to what happens for the generalized velocity, it will also depend also on the external action A ; furthermore, it will not vanish with the generalized velocity; the latter going to zero, the action of friction will tend to a positive value g .

In order to govern the motion of the system, we will no longer have a unique equation, but two distinct equations; the first of these should be used only when the generalized velocity $\dot{\alpha} = d\alpha/dt$ is positive; it will take the following form:

$$A + J + v - f = \frac{\partial F}{\partial \alpha}. \quad (4)$$

The second of these equations will read:

$$A + J + v + f = \frac{\partial F}{\partial \alpha}. \quad (4b)$$

This one will be reserved to the case when the generalized velocity $\dot{\alpha} = d\alpha/dt$ is negative.

As to the equilibrium condition, it will no longer be represented by an equality, but by a double inequality that expresses that the absolute value of the difference $A - \partial F/\partial \alpha$ is not larger than g :

$$-g \leq A - \frac{\partial F}{\partial \alpha} \leq g. \quad (5)$$

We rapidly go over the equation of living forces [equation of kinetic energy]; we can only repeat here practically all what was said when studying the dynamics of Helmholtz; it is only necessary to add the work of friction to the work of viscosity. The former, like the latter, is always negative. We also do not deal with the Clausius inequality which remains exact in the new dynamics. Here also, the work of friction is just being added to the work of viscosity. Other consequences of the laws just formulated, and more particularly the condition of equilibrium, will require a little more attention.

Gibbs' statics would require the difference $A - \partial F/\partial \alpha$ to vanish, and therefore having value between $-g$ and $+g$. The equilibrium states predicted by this Statics, and that are usually called states of *true equilibrium*, are thus among those that are

predicted by the new Statics; But the latter announces the existence of an infinity of other equilibrium states, that we designate by the name of *false equilibria*.

If the value of g is large, then the states of false equilibrium spread on both sides of those of true equilibrium, in a large domain. They will shrink close to the states of true equilibrium whenever the value of g is small. If this value becomes sufficiently small, then the states of false equilibrium will be so close to those of true equilibrium that experiments would no longer distinguish them; practically, the Statics of systems with friction would be undistinguishable from Gibbs' statics.

This is only a particular application of the following remark: Gibbs' Statics and Helmholtz' Dynamics are limit forms of the Statics and Dynamics of systems with friction; these tend to those when the action of friction becomes infinitesimally small.

This remark is not a simple view of the mind; it acquires a particular interest in the study of chemical equilibria¹.

Note 1. We have given an exposition of the theory of chemical equilibria accounting for friction and the principal applications of this theory in the following works: *Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques*, Paris, 1896 – *Traité élémentaire de mécanique chimique fondée sur la thermodynamique*, Vol. II, T. I, Paris, 1897; *Thermodynamique et chimie, leçons élémentaires à l'usage des chimistes*; Leçons XVII, XIX and XX, Paris, 1902.

[In the rest of this Chapter Duhem expands an example from chemical physics].

II. Permanent alterations and hysteresis

[Here Duhem first gives a general idea of what permanent alterations are. He emphasizes the role of infinitesimally slow evolutions, adapting accordingly temperature and external actions]

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[From page 421]

The theory of systems capable of permanent alterations will thus be distinct from general mechanics for which, with Gibbs and Helmholtz, we have sketched the principles; but it will also differ from the mechanics of systems with friction; it will be a new branch of mechanics.

How is this new mechanics to be constituted?

Only the principal thought is of concern to us here; the detail of formulas is not needed; we restrict ourselves to the study of a simple case that will allow for a better transparency of the frame of ideas. As object of our analysis, let us choose a system defined by a single normal variable, apart from temperature; for example a thread [wire] under tension of which the length will be this normal variable, while the pulling weight will be the corresponding external action.

First let us give certain infinitesimal variations to the temperature and the pulling weight; the length of the thread will suffer an infinitesimally small increase. Then let us give to both temperature and pulling weight variations equal in absolute value to the preceding ones, but with opposite sign so that these two quantities recover their original value. The length of the thread is reduced, but this

decrease does not have the same absolute value as the preceding lengthening, because the thread suffers a permanent deformation. Thus, in the course of an infinitely slow alteration, a linear algebraic relation determines the infinitely small variation of the length of the thread when we impose infinitely small variations to temperature and pulling weight; but this relation must not have the same form when the thread elongates or when it contracts; a certain equality must be written when the normal variable suffers a positive variation, and another one when this variation is negative.

What guide will help us to discover the form of these two equalities? It is the theory itself, which cannot be sufficient to treat permanent alterations, but which proved to be so fruitful in the study of systems with reversible modifications. We shall look for a construction of this new mechanics in such a way that it is as close as possible to that theory, that it follows from it by a very slight transformation, that it be one of its generalizations, that the Statics and Dynamics of systems admitting no permanent alterations be regarded as limit forms of the Statics and Dynamics of systems with very weak permanent alterations. In a nutshell, we shall follow the same method as that which was given by the theory of systems with friction.

When a system presenting no permanent alteration is subjected to an infinitely slow modification, i.e., a reversible evolution, the equilibrium conditions are satisfied at each instant; if the state of the system depends on a single normal variable α , then at each instant the external action A equals the derivative of the internal potential F with respect to α ; this we are taught by equality (1) [i.e., $A = \partial F/\partial\alpha$]

For coordinated infinitely small variations of the temperature, the external action and the normal variable, there therefore exists the relation

$$dA = d\frac{\partial F}{\partial\alpha}, \quad (6)$$

by virtue of the fact that the always equal quantities A and $\partial F/\partial\alpha$ suffer simultaneously equal increases. According to this relation, if we change the sign of these variations without changing their absolute value, then we change the sign of the variation suffered by the normal variable without changing its own absolute value; this way we express the reversibility of the infinitely slow modification.

These peculiarities cannot be met in a system capable of permanent alterations; each of the elements of which the succession composes an infinitely slow modification cannot be governed by equality (6); we must substitute to this equality two distinct relations, one valid when the normal variable increases, and the other valid when this variable decreases.

In the first case, we substitute to equality (6) the relation:

$$dA = d\frac{\partial F}{\partial\alpha} + h d\alpha, \quad (7)$$

In the second case, we substitute to (6) the relation

$$dA = d\frac{\partial F}{\partial \alpha} - h d\alpha. \quad (7b)$$

The quantity h , of which the introduction in these equations distinguishes systems capable of permanent alterations from those not capable of these, depends on the state of the system, and also on the external action A .

It is obvious that it suffices to give to this quantity h a very small value so that inequalities (7) and (7b) differ very little from the equality (6); the permanent alterations of the system then are very little sensitive, and its infinitely slow modifications are almost reversible; thus, systems without permanent alterations and capable of reversible modifications are precisely limit forms of systems subjected to small permanent alterations.

For systems without permanent alterations, a simple rule allows us to deduce from the internal potential the knowledge of the internal energy, and thus, the quantity of heat involved in an infinitely slow modification. Nothing forbids the extension of this rule to systems with permanent alterations. Joint to what was previously given, it will provide the essential principles on which the Statics of such systems relies². With some accessory hypotheses, all inspired by the desire to make the small branch ("rameau") of Thermodynamics as similar as possible as its master branch, this will complement these principles.

Note 2. We have devoted six memoirs to this Statics under the general title: Les déformations permanentes et l'hystérésis (*Mémoires in-4° de l'Académie de Belgique*, t. LIV, 1895; t. LVL, 1898; t. LXII, 1902) and eight memoirs published under the title: Die dauernden Aenderungen und die Thermodynamik, *Zeitschrift für physikalische Chemie*, Bd. XXI, XXIII, 1897; XXVIII, 1899; XXXIV, 1900; XXXVII, 1901), etc.

What are the applications of this new Statics?

A first category of permanent alterations is formed by elastic deformations. The traction, torsion and flexion cause deformations that do not disappear with the cause that produced them; these deformations, known and observed at all times since Antiquity, find in the above given principles, their theoretical explanation.

[Here Duhem mentions examples from residual magnetization, magnetic hysteresis, and analogous properties for electric polarisation in dielectrics].

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[continued from p. 422].

Essential as it is in the study of elasticity and the theory of magnetism, hysteresis is destined to play a very important role in "chemical mechanics"

It is without doubt to permanent alterations of this kind that must be attached the effects of tempering, annealing, and hardening that complicate so strangely the study of metals and their industrial combinations. Quite often, these effects result from both elastic hysteresis and chemical hysteresis; only the simultaneous consideration of these two hystereses, can somewhat untangle these phenomena, in appearance inextricable, that present some bodies; such as Nickel based steels of which M. Ch.-E. Guillaume has analyzed the strange properties, or the platinum-

silver alloy of which the electric resistance manifests so curious residual variations, as observed by M. H. Chevallier.

This superposition of chemical hysteresis and elastic hysteresis makes the laws of dilatation of glass singularly complex; the observation of the displacement of the zero point of thermometers had not revealed, first to Desprez and then to M. Ch.-Edmond Guillaume much more than this extreme complexity; numerous and patient measurements, guided by the thermodynamics of permanent modifications, have finally allowed M. L. Marchis to put some order in this chaos [Guillaume, Chevallier, Desprez and Marchis were doctoral students of Duhem in Bordeaux].

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[continued from page 423]

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In a system subjected to permanent alterations, the quantity h , that we name *coefficient of hysteresis*, does not vanish in general. The two equalities (7) and (7b) are thus distinct from one another; if we suppose that the system suffers, with an infinite slowness an infinitely small alteration due to certain variations in the temperature and the external action, we will not be able, by inverting those variations, to reverse the modification and to bring the system back to its initial state.

But what is not generally true may become true in certain particular cases; by associating in an appropriate manner the values of the normal variable, of temperature and of the external action, we can make the coefficient of hysteresis vanish; when these values are thus associated, we say that the system is placed in a *natural state*; in general, if we take the system in any state, defined by a certain value of the normal variable and a certain value of temperature, we can submit it to an external action so that this state becomes a natural one.

[Here Duhem goes more deeply in the notion of natural state and that of residual fields, and then he discusses the possible dynamics in which the standard application of d'Alembert's principle is at fault, referring to works by Henri Bouasse (1866-1958; a French physicist in Toulouse, South-west of France) and the noted German physicist Max Wien (1866-1938)].

III. Electrodynamics and electromagnetism

[In this long section, pp. 424-427, Duhem considers the general thermodynamics of electromagnetic bodies. He ponders the notions of electromagnetic energy, electric displacement, electromagnetic induction, electrodynamic forces, properties of the system which have no inertia associated with the relevant variables, in spite of the existence of generalized velocities duly associated with such variables, electrodynamic potential, electrokinetic energy, Ohm's effect considered as a viscosity. He pays an emphatic tribute to Helmholtz. He clearly expresses his irreconcilable appraisal of Maxwell's vision. This, of course, appears to be outdated and certainly not very objective].

Conclusion (pages 427-429).

[Here Duhem offers a rather literary synthesis of the contents of the whole work. He goes all the way to compare the construction of his successive theories to the "sanguine sketches" of Raphael on exhibit at the Louvre [museum] where you can see the work by successive approximations of this master painter, starting from a rough sketch and then improving the details at each successive picture and finally producing a masterpiece that finally causes the admiration of all. This is the way his new Mechanics, unique though complex, emerges from his own mind].

[continued from page 428, 2nd column]:

The old Mechanics pushed to the extreme the simplification of its fundamental hypotheses. It had condensed these hypotheses in a unique presupposition: All systems are reducible to a set of material points and solid bodies which move in agreement with Lagrange's equations. And even more with Hertz, it went further by erasing real forces from its equations.

The new Mechanics [i.e., Duhem's] is not imbued of such a simplification of its principles; it does not avoid to increase the complication of its fundamental hypotheses; it admits terms of varying nature and form in its equation, terms of viscosity, friction, hysteresis, electro-kinetic energy, while the old Mechanics excluded from its formulas such symbols, as in contradiction with its unique principle.

But reality is more complex, infinitely so; each new improvement in experimental methods, by scrutinizing more thoroughly the facts, discovers in them new complications. Human mind, in its weakness, although trying hard to work toward a simple representation of the external world, suffices to place the image in front of the object and to compare them in good faith in order to realize that this simplicity, so forcefully desired, is an un-captured chimera, an unrealizable utopia.

.....

[continued from page 429, first column]:

This capability to mould facts and to capture their finest detail was acquired by the new Physics by giving up some of the requirements that rigidified the old Mechanics. Among these requirements, the first and most essential one was the one that intended to reduce all properties of bodies to quantities, figures and local motions; the new Physics rejects totally this requirement; it admits in its reasoning the consideration of these qualities; it endows the notion of motion with the generality that Aristotle granted to it. This is the secret of its marvellous compliance. Indeed, with this it gives up the consideration of hypothetical mechanisms that the natural philosophy of Newton disliked, the research of the masses and hidden motions of which the only object is to explain the qualities in geometrical terms. Freed from this work that Pascal proclaimed uncertain, painstaking and useless, it can, in all freedom, devote its efforts to more fruitful endeavours.

.....

The creation of this Mechanics, based on thermodynamics, is thus a reaction against atomistic and Cartesian ideas – not foreseen by those who most contributed to it – to the deepest principles of peripatetician doctrines.

.....

The expansion of Mechanics is thus a true *evolution*; each stage of this evolution is the natural corollary of previous stages; it is pregnant of future stages. The meditation of this law must me the comfort of the theoretician. It would be presumptuous to imagine that the system toward which he contributes will escape the common fate of systems that were before, and will deserve to last longer than them; But, without any vain verbiage, he is right in thinking that his efforts will not be sterile, that across centuries the ideas that he sowed and made germinate, will continue to grow and bear fruits.

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