Chapter 7 Helmholtz Interpreted and Applied by Duhem

Abstract Gibbs and Helmholtz provide the strongest scientific influences on Duhem's works in what is now called *mathematical physics*. With the help of examples exhibiting this influence in thermo-mechanics and electrodynamics, it is shown that this conduced Duhem and his followers to a definite style and practice of physical science marked by abstraction and mathematical rigor. This has practically become the rule while helping to classify the numerous, linear or non linear, effects and giving rise to fruitful developments, in continuum physics.

7.1 Hermann von Helmholtz and Pierre Duhem

When Hermann von Helmholtz (1821–1894) dies in Berlin in 1894, the same year as Heinrich Hertz of electrodynamics fame, Pierre Duhem (1861–1916) is only thirty three years old and moving from one teaching position in Rennes to a professorship of theoretical physics at the University of Bordeaux.¹ But he has already published in 1886 one of his most original books [\[9](#page-11-0)], a short treatise on thermodynamic potentials and their application to what he calls ''chemical mechanics'' and electric phenomena. This book appears to be some kind of matured rewriting of an aborted thesis project which he wrote and presented in

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¹ Excellent biographical sketches of P. Duhem are given in Jaki $[31]$, Brouzeng $[4]$ $[4]$, and Miller [[42](#page-12-0)]

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1884 while being a third year student at the celebrated *Ecole Normale Supérieure*, having not yet obtained his formal Master's degree, nor passed the difficult competition exam called the Agrégation (formally, Lycée teaching diploma). Unfortunately for Duhem, this project included a somewhat harsh argument against Marcellin Berthelot, then ''Pope'' of French ''republican'' physics, but conceptor of the ill-fated principle of maximal work, whereby the heat of reaction defines the criterion for the spontaneity of chemical reactions. Rightly, but perhaps without the respect and touch of hypocrisy that would have been more suited in such occasions Duhem, building on of the notion of free energy dear to Helmholtz and also known to J. W. Gibbs who called it "available energy", denounced Berthelot's theory as a fraud, and properly defined the required criterion in terms of the free energy. The thesis was rejected. An enmity between Berthelot and Duhem followed from which Duhem never fully recovered, having his academic career impeded for his whole life. Duhem obtained his doctoral degree with another subject (theory of magnetism) and a different jury (involving Henri Poincaré) in 1888.

Pierre Duhem, like many other physicists of the period, was interested in the whole of phenomenological physics, the physics of his time—a pre-quantum time -, and was particularly keen on problems of electromagnetism and electrodynamics. With the discovery of Heinrich Hertz about electromagnetic waves and his will to capture the whole of physics in a somewhat rigorous framework, he turned to the study of the foundations of the theory of electrodynamics. His rapid conclusion was that Maxwell's work was more the work of an inspired artist than that of a logician (which Maxwell had never claimed to be) and if something deserved the respect of a true mathematician or mathematical physicist, it was the electrodynamic theory set forth by Helmholtz, although perhaps there was more in it than necessary (see below). While Poincaré [\[44](#page-13-0)] exposed all theories in a detailed, cautious and balanced manner—which announces his conventionalism in his lectures at the Sorbonne, Duhem, true to himself, wrote a pamphlet against Maxwell [\[14](#page-11-0)] in which he had to acknowledge Maxwell's obvious genius and ingenuity (in introducing the notion of displacement current) while exposing his sloppiness to the scientific world: Maxwell achieved something great, but not in a form admissible to a professional of mathematical physics. This is the viewpoint that Duhem was to illustrate first on this particular example, and that some irrational nationalistic tendencies were to develop in an open attack of the English way of practicing science, and where German (in particular Helmholtz) and obviously French science got the best share in an analysis which was nonetheless to bring an original and creative viewpoint in epistemology [[15\]](#page-11-0).

A few years before his untimely death in 1916, Duhem [[16\]](#page-11-0) published a formidable treatise on *energetics* or *general thermodynamics* in which he naturally praised the German school of energetics in which Helmholtz was incorporated as a precursor. Furthermore, basing on the concept of free energy, this beautiful work presented a thorough discussion of stability which would sixty years later be taken over by a whole school of continuum thermo-mechanics. That school, under the leadership of Clifford Truesdell, developed, at the image of the best analysts of the

nineteenth century and Duhem himself, a rational approach which, like all ''rigidifications'', was instantaneously fruitful but may have brought some damage in the long run (think of the Bourbaki style in mathematics). Here also, Duhem had a debt to Helmholtz via Hertz and his enterprise of rationalization of mechanics as shown in his small book on the principles of mechanics [\[27](#page-12-0)]. From this we gather that Helmholtz inspired or for the least shared, some of the views expressed by Hertz, especially in using Hamilton's dynamic principle. This was to develop in a true *theory of fields* in which the notion of force would ultimately be banished.

In the remainder of this contribution we shall examine in greater detail the four instances and subject matters at which the intellectual trajectories of von Helmholtz and Duhem clearly crossed each other. These views, methods, attitudes toward scientific practice, sometimes only hinted at by Helmholtz and more forcefully expressed by the sanguine Duhem, have necessarily influenced our own practice and our view of *mathematical physics* in general and the way we teach it and write papers in particular; That is, a style has developed which has built on the peculiarities exhibited by our grand predecessors. This is all the more true in a field such as *continuum thermodynamics* which may rightly be considered as a modern expression of energetism, but without the limitations and blinkers too often put forward by its contempters.

7.2 Free Energy (''Freie Energie'')

Nowadays all our (good) students know the difference between internal energy and free energy, the latter being also called *Helmholtz energy*, although no personal name seems to be attached to the former, being more the result of collective thinking and appraisal. They essentially know when each of these prevails in the thermodynamic description of systems, for isentropic conditions in the first case, isothermal ones in the second case. This obviously has drastic consequences even in the most modern researches and applications of thermo-mechanics. For example, while P. Hugoniot (1851–1887) clearly shows the relationship between his celebrated jump conditions across shock waves and the notion of internal energy (work generalized by P. Duhem himself in 1901), coherent transition fronts in elasticity, describing transitions of the martensitic-ferroelastic type in conductors of heat, involve the free energy of the deformable material, hence a function of strain and temperature, as shown by the author and co-workers. $²$ That is, the</sup>

$$
H := [e + \langle p \rangle \tau]
$$
 (a)

 $2\;$ In shock waves for one-dimensional motions in fluids the *Hugoniot jump relation* reads

where $e(\tau, \eta)$ is the *internal energy* per unit mass, a function of specific volume τ and specific entropy η ; p is the thermodynamical pressure, $\theta = \partial e / \partial \eta > 0$ is the thermodynamic temperature, $\langle \ldots \rangle$ is the mean value of a quantity at the shock, and [..] its jump. The best known disciple of Duhem was E. Jouguet, a specialist of shock and detonation waves, and explosives.

driving force acting locally on the transition front is essentially the jump in free energy, or a quantity akin to that. The same holds true for electromechanical or magneto-mechanical transition fronts. In contrast, for shock waves, whether in solids or in fluids, it is the internal energy, function of strain or volume and entropy which provides a basis for a discussion of the existence of shocks by means of the so-called *Hugoniot function*. Duhem was instrumental in these developments through his teaching and the introduction of several welcomed concepts. Apparently, he pondered such questions as that of thermodynamic potentials while still in secondary school/gymnasium under the supervision of his physics teacher Jules Moutier. The works that he expanded in the period 1884–1900 in this field clearly are extensions and elaborations of the pioneering work of Gibbs and Helmholtz. He had read both authors while in college, especially the first part of Helmholtz [\[25](#page-12-0)]. He was also quite aware of the work of the French geologist François Massieu (1832–1896). It is him who gave to Massieu's characteristic functions [\[34](#page-12-0)] the name of *thermodynamic potentials*, while he treated systematically all types of thermodynamic systems involving as well thermoelectricity, capillarity, mixtures of perfect gases, those of liquids, solutions in gravitational fields and magnetic fields, freezing points, etc.

Duhem acknowledged his immense debt to Gibbs and Helmholtz when, in Duhem [\[17](#page-11-0)], he described in detail his scientific trajectory in the presentation of his works while a candidate for election to the Paris Academy of Sciences. In the 1960s, the Truesdellian-Nollian school of rational thermodynamics took over the axiomatic approach of Duhem to introduce a priori in full dynamics notions which are usually defined only in thermostatics, e.g. temperature, entropy, and free energy. Much celebrated papers by Coleman and Noll [[8\]](#page-11-0) in fact introduced the statement of the second law of thermodynamics in which the time rate of change of free energy is present as the so-called Clausius-Duhem inequality, a mathematical restriction imposed on a large class of material behaviors.³

But in his pursuit of a general thermodynamics that started with a full exploitation of Helmholtz' freie Energie, Duhem accomplished much more in that he also introduced seminal notions and powerful methods which were to bring efficient results in the second part of the twentieth century. Among the methods we

$$
F = -[W(\varepsilon, \theta) - \langle \sigma \rangle : \varepsilon]
$$
 (b)

⁽Footnote 2 continued)

For one-dimensional phase-transition fronts (this dimensionality is chosen for illustrative purpose only) in solids, the *driving force* acting on the front reads:

where W is the free energy per unit volume, a function of strain ε and temperature θ , the entropy per unit volume is given by $S = -\partial W/\partial \theta$, and σ is the stress. $H = 0$ at shocks whereas F is in general not zero at irreversibly progressing phase-transition fronts. Both F and the nonzero propagation velocity V of the front satisfy jointly at the front the second law of thermodynamics in the form $F.V > 0$ or $= 0$ (for the exact three-dimensional theory in conductors of heat see [[39](#page-12-0)]).

 3 Much more on rational thermodynamics is to be found in Truesdell [\[46\]](#page-13-0).

should emphasize the systematic use of *Euler's theorem for homogeneous func*tions.⁴ The celebrated Gibbs-Duhem equation, of relatively innocent outlook in our much more mathematically trained society, was the result of this use. It may not be altogether ridiculous to recall that this technique reduces the derivation of relations among partial molar properties of a solution to the repeated application of this theorem. Among the notions unequivocally introduced by Duhem we find those of normal variables of state and the embryonic form of what was to become known as internal variables of state in recent times. Normal state variables are composed of a set including entropy and a remainder set $\{ \chi_{\beta}; \beta = 1, 2, ..., n \}$ according to which the first law of thermodynamics in Gibbs' form can be expressed as

$$
dE = \omega + \varphi \tag{7.1}
$$

where ω and φ are the elementary work and heat received by the system in such a way that

$$
\varphi = \theta \, dS, \quad \omega = \sum_{\beta=1}^{n} \tau_{\beta} \, d\chi_{\beta}, \tag{7.2}
$$

where S is the entropy and the τ'_{β} s are thermodynamic forces associated with the χ'_{β} s. That is, there is **no** dS in ω and this, together with the positiveness of the dual variable, the temperature θ , makes S singular among the state variables. Indeed, E, the internal energy, is a thermodynamic potential in the sense of Duhem, in such a way that

$$
\theta = \partial E / \partial S, \quad \tau_{\beta} = \partial E / \partial \chi_{\beta} . \tag{7.3}
$$

Manville [\[32](#page-12-0), p.225], in assessing Duhem's contribution to thermodynamics, says that Duhem based on an idea of Helmholtz while introducing the notion of normal variables.

Although Duhem was not equipped to solve the problem of what he called the "nonsensical" (abérrantes) branches of mechanics—those branches where *dissi*pation is the most important mechanism at play, one may find in some of his penetrating writings [[12\]](#page-11-0)—cf. Manville [[32\]](#page-12-0), p. 303; Truesdell [\[46](#page-13-0)], p. 39—the germ of the notion of internal variable of state. Without digressing too much on this we simply note that these are additional variables of state whose introduction reflects our lack of complete control of microscopic mechanisms (e.g. dislocation movement) which are responsible for some macroscopically irreversible manifestations (e.g. plasticity and hardening in metals, magnetic hysteresis in ferromagnets). Although measurable by a ''gifted'' experimentalist once they have been identified (this is the crux of the matter), these variables are not *controllable* so that they clearly distinguish themselves from the more classical observable

⁴ This is rightly emphasized by Miller [\[42\]](#page-12-0), p. 229.

variables of state that are controlled by body or surface actions—cf. Maugin and Muschik [\[38](#page-12-0)] for a lengthy analysis.

By gathering the properties of *convexity*, *Euler's* identity for homogeneous functions of degree *n*, the powerful notion of *Legendre transform* and more generally Legendre-Fenchel transform, normal variables and internal variables with the local statement of the second law that carries his name, we are now able to formulate in a coherent, mathematically correct, and efficient manner a true thermo-dynamics of complex irreversible processes of which Duhem could only dream of. To achieve this, the school of de Donder, Prigogine, Meixner, de Groot and others had, in the mean time, to formulate the second law in an operative form, the celebrated bilinear (in ''fluxes'' and ''velocities'') form of the dissipation *inequality* (which is not limited to linear dissipative processes as too often advertised). Also potent in these developments was the axiomatization of ther*mostatics* by Caratheodory [\[6](#page-11-0)] and Born [\[2](#page-11-0)]; here also, with Miller $[42, p.229]$ $[42, p.229]$ $[42, p.229]$, we must reckon the pioneer role of Duhem [\[10](#page-11-0)] who essentially gave the correct definitions relating to the first law [see above Eqs. (7.1) (7.1) (7.1) – (7.3) (7.3) (7.3)], what marks the true beginnings of the axiomatization of branches of science outside pure mathematics. Duhem paid a special tribute to Helmholtz in this regard (see Duhem [\[17](#page-11-0), p. 75]; also Duhem $[16]$ $[16]$). Nowadays, most teachers of continuum thermo-mechanics⁵ follow in their practice the grand avenue opened by Clausius, Helmholtz, Duhem, Caratheodory and, more recently, among others, P. Bridgman, J. Kestin, C. A. Truesdell, W. Muschik, and I. Müller.

7.3 Helmholtz-Duhem Electrodynamics

One uncompleted project of Pierre Duhem was the incorporation of electricity and magnetism, including nonlinear dissipative effects such as hysteresis, in his broad energetic view. This he never achieved as bears witness his monumental treatise of 1911. But in his search for this development he inevitably faced the various theories that were available in his time.

If we make exception of the early French and Italian works (Coulomb, Poisson, Ampère, Mossotti), we find essentially two avenues along which electromagnetism developed: one led by Faraday in England, which gave rise to W. Thomson's (Kelvin) and Joule's works, and Maxwell's brilliant synthesis and further devel-opments by the "Maxwellians" (Cf. [[30\]](#page-12-0)), the other in Germany with, after Gauss, people like Neumann, Kirchhoff, Weber, Riemann, and Helmholtz. In other words,

⁵ This is exemplified by the author's course that deals with strongly nonlinear dissipative processes Maugin [[36](#page-12-0)]. This style of thermodynamical exposition is to be found in the *Journal of* Non-Equilibrium Thermodynamics, de Gruyter, Berlin. The book by Bridgman [[3\]](#page-11-0) was instrumental in this development, especially in influencing Joseph Kestin from whom we all more or less learned our ''thermodynamics''. The points of view of Duhem, Bridgman and Kestin are examined in parallel and comparison in the book [[37](#page-12-0)].

in the scrutiny of, at the time, recent works, Duhem was confronted with scientific works expanded in various cultural and educational backgrounds and environments that differed from the French one, different ''national styles'' following one of his favorite expressions. It is probably during this thorough analysis of available works that he realized how different were the attitude and practice of various scientists in forming ideas, conceiving models in general, and assessing the role of scientific constructs.

Like all potential readers, and the few who indeed passed to the act, Maxwell's [\[40](#page-12-0)] treatise on electricity and magnetism seemed to Duhem to be full of contradictions, non rigorous developments, errors in sign, and lacking true experimental foundations (a point Duhem emphasized in spite of his own tenuous contact with experiments). The main question is whether we can reach the mathematical form of physical laws through mere divination, helped in this by a strong inclination towards aesthetics and a love of symmetry, or through a logical unwinding of arguments of which pure mathematics offers a paragon (in its final written form at least) with a view to reflect, but not to explain, physical reality; to "save the phenomena'' according to Plato's celebrated formula. In Maxwell, his ''bête noire"', and perhaps even more in W. Thomson (Lord Kelvin), Duhem detects the prototypically British ''ample and shallow'' mind (Duhem [\[15](#page-11-0), Chap. 4]). According to Duhem, this, obviously, unfavourably compares with the typically French "narrow and deep" scientific mind which he naturally considers to be far more superior in so far as scientific development is concerned; this despite all evident successes and creativity of British physics in the nineteen century! The fact that we find both types on both sides of the Channel (to him the French mathematical physicist Boussinesq belongs to the ''British'' class, op. cit. p.89) did not deter Duhem from his general ''theory'' which, therefore, must be considered in a true statistical way. The irony of all this is that finding an electromagnetic theory to his own taste in the German background, especially in the form expanded by Helmholtz in the 1870s, Duhem generously classified German science on the French "narrow-deep" minded side: "To a Frenchman or a German, a physical theory is essentially a logical system'' [[15,](#page-11-0) p. 78]. This is to be considered a compliment in the mouth of Duhem. With the explosion of World War One, he changed his mind towards most German scientists whom he then relegated in the rigourless ample-shallow type, but for a few exceptions such as Helmholtz. That does not sound very serious at all.

More seriously, it is true that the introduction of the displacement current in electrodynamics always looks like *magic* to the inexperienced observer.⁶ Thanks to it, some symmetry is established between electric and magnetic phenomena, from which there results a wave equation, with finite speed of propagation for electromagnetic waves. The latter are purely transverse as experimentally checked

 6 Duhem $[15,$ English translation, p. 79] claims that Maxwell justifies the introduction of the displacement current by means of two lines:'' The variation of the electric displacement should be added to the current in order to obtain the total movement of the electricity''.

by Hertz in 1888. By the same token optics was given a full electromagnetic basis. At this point it may be relevant to remind the reader that most researchers in elasticity theory in the 1820s–1840s (e.g. G. Green and A. L. Cauchy who were perfect models in Duhem's view of mathematical physics) were motivated by the construction of a model of continuum capable of supporting transverse vibrations at it was already known that luminous vibrations in transparent media are essentially transverse (cf. A. Fresnel), while the only continuum whose behavior was well understood before the introduction of the notion of *stress* (tensor) could only support longitudinal vibrations (acoustic waves in the most restricted way).

Now back to Helmholtz and to what Duhem considers a good logico-deductive construct, one that does not disturb the French and German minds. Helmholtz,⁷ himself dissatisfied with Maxwell's approach, proposed an electromagnetic theory which precisely allows for the propagation of both transverse *and* longitudinal perturbances. An extra parameter (compared to Maxwell's framework) thus appears in that theory. If it is true (in fact a discussed matter) that, by an appropriate choice of values of parameters, Maxwell's equations appear as a special case of Helmholtz's theory—i.e. transverse fluxes propagate with the velocity of light if one adopts the Faraday-Mossotti hypothesis, Duhem, in the faith of experiments which proved to be wrong, believed that there were experiments showing that longitudinal fluxes can also be propagated, at the velocity of light as well, this fixing the value of Helmholtz's additional parameter. We all know that Max well's equations"—as Hertz and Heaviside liked to call Maxwell's theory in a reductive manner—have triumphed. But it is still believed that the logical derivation of Maxwell's equations from a continuum point of view comes best through what Miller [\[42](#page-12-0), p. 231] definitely calls the "Helmholtz-Duhem" theory with the proper choice of constants.⁸ More than this precise derivation, it is perhaps the general attitude towards theoretical constructs which should bring some lesson

$$
\nabla^2 \mathbf{U} = (1 - k) \nabla (\partial \phi / \partial t) - 4\pi \mathbf{J},
$$

\n
$$
\nabla \cdot \mathbf{U} = -k \partial \phi / \partial t ,
$$

\n
$$
\nabla^2 \phi = -4\pi \rho_f, \quad (\partial \rho_f / \partial t) + \nabla \cdot \mathbf{J},
$$

⁷ This is mainly exposed in Helmholtz $[24]$ $[24]$ $[24]$ —also (Helmholtz $[26]$ $[26]$ $[26]$, posthumous). In modern times, this theory has been discussed several times, e.g. by Hirosize [\[29\]](#page-12-0) and Buchwald [\[5,](#page-11-0) see Chap. 21]. Strangely enough, none of the modern commentaries cites Duhem's thorough analysis, perhaps because Duhem went through some purgatory period and the original work in French was never reprinted or translated. For the information of the reader, Helmholtz's equations using potentials read (in modern notation).

where U and ϕ are a vector potential and a scalar potential, and k is a constant to be found by means of experiments conducted on an open circuit. It is to be noted that the time rate of change of ϕ affects U by virtue of the continuity equation. This, in fact, is a hindrance in the reduction of Helmholtz' to Maxwell's equations. We recommend Buchwald's discussion as very enlightening, especially in so far as the ''Maxwell limit'' is concerned. Duhem's analysis is also briefly given in his Duhem [\[17,](#page-11-0) pp. 147–150].

⁸ This is contended by Roy $[45]$ $[45]$ $[45]$, and. O'Rahilly $[43]$, Chap. [5](#page-11-0)]; See also Buchwald $[5]$, Chap. 21].

especially in teaching practice or in establishing well-framed mathematicalphysical theories.

Duhem [\[17](#page-11-0), pp. 147–150] comments that the superiority of Helmholtz's electrodynamic doctrine stems from its application of logical rules of thought, a standpoint that Poincaré [\[44](#page-13-0)], Hertz [\[28](#page-12-0)], and Boltzmann [[1\]](#page-11-0) seem to share to some extent. His attitude towards mathematical rigour and generalization are reflected in many formal approaches to continuum physics, in particular thermodynamics, in the 1960s–1980s, essentially through the works of the Truesdellian-Nollian school and its imitators. A concern to be as general as possible and a fear to miss an effect or coupling, how small it may be, are thus responsible for an inflation in length and breadth which is not commensurate with to the obtained results. The introduction of the so-called "*principle of equipresence*"⁹ in the formulation of constitutive equations by C. A. Truesdell, although a useful guideline in several cases, reflects this kind of abuse and often un-necessary generality, the said principle being violated or negated in many cases (hence not a principle at all, at most a precautionary measure). The same holds true of the manifested will to introduce as wide as possible classes of constitutive equations which are *functionals* over elapsed time (hereditary processes) and space (strong nonlocality). In many instances, these can be dispensed with from the beginning with some physical insight which has nothing to do with Maxwell's magic, but is closely related to his ingenuity.

7.4 Stability

Largely under the influence of Gibbs, a life concern and recurrent research theme of Duhem has been the stability of equilibrium for a variety of circumstances. He synthesized his results on this and his general theory about it in his treatise on energetics of 1911. In this ambitious endeavour, as we know now in pure mechanics, potential energy plays a fundamental role. Therefore, in a thermodynamic background, it is the thermodynamic potentials, Helmholtz's freie Energie or the available energy of Gibbs in isothermal systems, which capture the essentials of this property of stability. Early in his research Duhem concentrated on isothermal and isentropic stabilities of classical thermodynamics. He was very successful with sufficient conditions but much less with necessary ones. He tried to extend his results to all types of continua including elastic bodies and viscous systems [[11\]](#page-11-0). But the difficulty was beyond the knowledge of the period. Such questions have in fact been rigorously resolved only recently. Coleman [[7\]](#page-11-0) and Ericksen [\[18–20](#page-12-0)] have been instrumental in dealing with these aspects of stability theory.

⁹ We remind the reader that this "principle" recommends to enter the *whole* set of independent field variables as possible arguments in all constitutive equations.

What is perhaps more striking is the visionary insight that Duhem brought to this study by showing familiarity with Lyapunov's works, although with some (forgivable) confusion. In that he pioneered the use of Lyapunov's functions that would become an essential ingredient in the modern studies of Glansdorff and Prigogine $[23]^{10}$ $[23]^{10}$ as the problem of the response of a system to spontaneous fluctuations is related to the Le Châtelier-Braun principle, itself clarified by Duhem's study of the displacement out of equilibrium. Even more striking is the fact that some of his studies on hysteretic phenomena clearly anticipate modern formulations of elastoplasticity or magnetic hysteresis by setting forth a local stability criterion of the Drucker type (this gives the sign of the slope at any point of the hysteresis response) and a global one (over a complete cycle—this in fact imposes the sense in which the cycle is described) of the Ilyushin type.¹¹ These studies, interesting and farsighted as they were, remained practically ignored until scientists interested in the general phenomenon of hysteresis re-discovered them.¹²

7.5 Conclusions

The influence of Gibbs and Helmholtz on Duhem's passionate interest in thermodynamics, on his general view of energetics, and in specific aspects of his research, is obvious.¹³ Regarding Helmholtz more particularly, we have already noted that Duhem inherited from him the notion of *free energy*, or more generally,

¹⁰ See Chap. 4 in Glandsdorff and Prigogine [[23](#page-12-0)] for the stability according to Gibbs and Duhem. The general theory of the stability of thermodynamic equilibrium makes use of the Gibbs-Duhem approach and the balance of entropy. Chapters 6 and 7 deal with systems out of equilibrium. The minimum property of the dissipation function has been established by Helmholtz for a linear viscous fluid. The relationship between the Le Châtelier-Braun principle and Duhem's work on the displacement out of equilibrium is reported in Manville [[32](#page-12-0), pp. 259–260].

 11 The original works of P. Duhem on hysteretic systems are published in 1901 in the Zeitschrift für physikalisch Chemie and in the Mémoires présentés à la Classe de Sciences de l'Académie de Belgique. The most relevant equations are best expressed by Manville [[32](#page-12-0)]—apparently the finest and sharpest analyst of Duhem's scientific works—e.g. his Eq. (9) in p. 310, dA .da > 0 , and his un-numbered equation in p. 313: Integral of A $da > 0$ for an isothermal closed cycle, are identical to the expressions of Drucker's and Ilyushin's local and global stability conditions of modern plasticity with hardening—compare to Eqs. (5.75) and (5.88) in Maugin [\[36\]](#page-12-0), pp. 108 and 111, respectively, where the proof relies on the convexity of the free energy with respect to a, and the convexity of the homogeneous positive dissipation potential in A, the thermodynamical force associated to a. This applies to so-called *generalized standard* (thermodynamic) materials whose two basic potentials (free energy and dissipation) exhibit these properties. Duhem did not possess the last concept but he had a rather clear view of incremental laws exhibiting hysteresis as shown by Manville's [[32](#page-12-0)] equations in pp. 307–310.

 12 Thus Duhem's works now belong in all respectable bibliographies on hysteresis, e.g. Visintin [[48](#page-13-0)] and Mayergoz [[41](#page-12-0)].

¹³ To Manville [[32](#page-12-0)], p. 197 Gibbs and Helmholtz are not dissociable in Duhem's vision.

thermodynamic potentials, that of normal variables of state, and elements of his general approach to the stability of equilibrium. Duhem saw in Helmholtz not only a forerunner of what he calls ''énergétique'', but also the prototype of what a good and efficient *mathematical physicist* should be. This is practically manifested in Duhem's reception of competing theories of electromagnetism in which he preferred Helmholtz's ideas, although quite forgotten today (but not in Duhem's time), to the somewhat ''amateurish'' presentation of Maxwell. This was not so much a matter of contents than one of presentation and interpretation. Duhem's and Helmholtz's views on the need for an abstract and logically ordered theory coincided more or less. Is it not Helmholtz^{14} who, writing the foreword to Hertz's Principles of Mechanics [[27\]](#page-12-0), confesses that ''I remain attached to this latter mode of presentation (''very general representation of facts and their laws by the system of differential equations of physics''), and I place more confidence in it than in the other (''mechanical explanations and models à la Maxwell-Thomson'').

In [\[14](#page-11-0), [15](#page-11-0)] Duhem sees Helmholtz's works as the ultimate step in "the developments which abstract theory has undergone from Scholasticism to Galileo and Descartes; from Huygens, Leibniz and Newton to d'Alembert, Euler, Laplace, and Lagrange; from Sadi Carnot and Clausius to Gibbs and Helmholtz'' (Duhem [\[15](#page-11-0)], p. 305). We surmise that this list would have been fully endorsed by C. A. Truesdell with the obvious addition of the marvelous Cauchy. A close examination of this list reveals that all participants concurred, although at different historical times, in creating what may be actually referred to as the *nonlinear* theory of fields in the sense of Truesdell and Noll [[47](#page-13-0)] or continuum physics in the sense of Eringen [[21\]](#page-12-0). In this, while adding his personal touch to many arduous points and innovating on specific problems, Duhem was an efficient intermediary between the last great ''all-round'' scientists of the nineteenth century and the continuum theorists of the late twentieth century, especially in continuum thermomechanics. As a talented and stubborn propagandist in the defense of this cause he was more than influential on our practice and vision of Isaac Newton in his own time. In lower spheres, all our teaching and research practice in continuum thermomechanics is inevitably marked by Gibbs, Helmholtz and Duhem, through the concept of free energy and the constant use of the *Clausius-Duhem inequality* as a constraint imposed on the evolution of all types of phenomena, including severely nonlinear ones. Thermo-elasticity, the theory of defects, the rheology of solutions of macromolecules, and the progress of phase-transition fronts make constant use of thermodynamic restrictions and styles of reasoning that belong to this line of scientists. In a hundred years, a message—that one that Helmholtz expressed vividly in his foreword to Hertz's text—has gone through: we practice mathematical physics in a definite style which is both serene and efficient, in a language that has become accessible to all scientists trained throughout the World. But we would like to add a very personal remark. It is commonly agreed with Duhem that a true ''scientific'' work in a field of natural science makes use of a concise

¹⁴ Cf. Hertz $[27]$, quoted by Duhem $[14, 15]$ $[14, 15]$ $[14, 15]$ $[14, 15]$, p. 100.

language, with accompanying concentrated objectivity and convincing logic; it must suppress feelings, do not digress into metaphysics, and do not try to find meaning beyond the visible phenomena. But literacy and a good sense of humour are not forbidden, for both author and reader must still share together that exquisite feeling of the true existential pleasure found in the practice of science.

References

- 1. Boltzmann L (1893) Vorlesungen über Maxwells Theorie der Elektrizität und des Lichtes, 2 volumes. Leipzig
- 2. Born M (1921) Kritische Betrachtungen zur traditionellen Darstellung der Thermodynamik. Phys Zeit 22:218–224, 249–254, 282–286
- 3. Bridgman P (1943) The nature of thermodynamics. Harvard University Press, Cambridge
- 4. Brouzeng P (1987) Duhem: science et providence. Belin, Paris
- 5. Buchwald JZ (1985) From Maxwell to Microphysics (Aspects of Electromagnetic Theory in the Last Quarter of the Nineteenth Century). The University of Chicago Press, Chicago [see Chap. 21]
- 6. Caratheorory C (1909) Untersuchungen über die Grundlagen der Thermodynamik. Math Ann 67:355–386
- 7. Coleman BD (1973) The energy criterion for stability in continuum thermodynamics. Rend Semin Mat Fis Milano 43:85–99
- 8. Coleman BD, Noll W (1964) Thermodynamics of materials with memory. Arch Rat Mech Anal 17:1–46
- 9. Duhem P (1886) Le potentiel thermodynamique et ses applications à la mécanique physique et à la théorie des phénomènes électriques. A. Hermann, Paris 248 pp
- 10. Duhem P (1893) Commentaires aux principes de la thermodynamique, Seconde partie: Le principe de Sadi Carnot et de R. Clausius. Journ Math Pures et Appl 9:293–359
- 11. Duhem P (1902) Sur les conditions nécessaires pour la stabilité de l'équilibre d un système visqueux. C R Acad Sci Paris 135:1290–1294
- 12. Duhem P (1903) Considérations sur la stabilité, et plus particulièrement la stabilité des corps élastiques. In: Procès verbaux des séances de la Société des Sciences Physiques et Naturelles de Bordeaux, 25 juin 1903 [also in: Recherches sur l'élasticité, Third part: La stabilité des milieux élastiques, 218 pages. Gauthier-Villars, Paris, 1906]
- 13. Duhem P (1903) L'évolution de la mécanique, 348 pages. A. Joanin, Paris [Collection of seven papers published in 1903 in the « Revue Générale des sciences Pures et Appliquées »]
- 14. Duhem P (1906) Les théories électriques de J. Clerk Maxwell Etude historique et critique, 228 pages. A. Hermann, Paris [This is a collection of papers published in 1900–1901 in the Annales de la Société Scientifique de Bruxelles]
- 15. Duhem P (1906) La théorie physique, son objet et sa structure, 450 pages. Chevalier et Rivière, Paris (This is a collection of papers published in 1904 and 1905 in the Revue de Philosophie). English translation: The Aim and Structure of Physical Theory, Princeton University Press, 1954; paperback edition 1991; precise references are to this edition; German translation: Autorisierte übersetzung: Ziel und Struktur der Physikalischen Theörien, mit einem Vorwort von Ernst Mach, 367 pages. Johan Ambrosius Barth, Leipzig (1908)]
- 16. Duhem P (1911) Traité d'énergétique ou de thermodynamique générale, Two volumes, 528 and 504 pages. Gauthier-Villars, Paris
- 17. Duhem P (1913) Notice sur les Titres et Travaux Scientifiques de Pierre Duhem, rédigée par lui-même lors de sa candidature à l'Académie des Sciences [Reprinted in: Mémoires de la Société des Sciences Physiques et Naturelles de Bordeaux, 7ème série, T. 1, pp 40–169 (1917)]
- 18. Ericksen JL (1966) Thermoelastic stability. In: Proceedings. 5th National Congress Applied Mechanics, pp 187–193
- 19. Ericksen JL (1977) Special Topics in Elastostatics. In: Advances in Applied Mechanics, Ed. C.-S. Yih, 17:189–244, Academic Press, New York
- 20. Ericksen JL (1991) Introduction to the thermodynamics of solids. Chapman and Hall, London
- 21. Eringen AC (Editor 1971–1976) Continuum Physics, Four volumes. Academic Press, New York
- 22. Eringen AC, Maugin GA (1990) Electrodynamics of Continua, Two volumes. Springer, New York [Soft-cover reprint, Springer, New York, 2012]
- 23. Glandsdorff P, Prigogine I (1971) Structure, stabilité et fluctuations. Masson, Paris
- 24. Helmholtz H von (1870) Über die Bewegungsgleichungen der Elektrizität für ruhende leitende Kôrper. (Crelle) J reine angewandte Math 72:57–129
- 25. Helmholtz H von (1882) Die thermodynamik chemischer Vorgänge. Sitz Deutsch Akad Wiss Berlin 1:22–39
- 26. Helmholtz H von (1897, posthumous) Vorlesungen über die Theorie des Lichtes. Unter Rucksicht auf. d. elastische und der elektromagnetische Ausschauung, J.A. Barth, Leipzig (Lectures)
- 27. Hertz H (1894) Die Prinzipien der Mechanik, in neuem Zuzammenhange dargestellt, Leipzig [English translation: The Principles of Mechanics, New York 1899; Dover reprint, New York, 1956]
- 28. Hertz H (1894–5) Untersuchungen über eine Ausbreitung der elektrischen Kraft. In: Vol. 2 of Gesammelthe Werke, Ed. P. Lenard, Leipzig
- 29. Hirosize T (1969) Origins of Lorentz Theory of Electrons and the Concept of the Electromagnetic Field. In: Historical Studies in the Physical Sciences, Ed. McCormmach, Vol 1, pp 151–209, Princeton University Press, New Jersey
- 30. Hunt BR (1991) The maxwellians. Cornell University Press, Ithaca
- 31. Jaki SL (1984) Uneasy genius: the life and the work of Pierre Duhem. Martinus Nijjhoff, The Hague
- 32. Manville O (1927) La physique de Pierre Duhem. In: Pierre Duhem, Sa vie Ses Oeuvres, Mém Soc Sci Phys Nat Bordeaux T.1, 7ème Série, pp 171–636
- 33. Manville O (1928) L'oeuvre scientifique de Pierre Duhem, Vol l, Bordeaux (see especially pp 71–76 for the scientific heritage of Helmholtz)
- 34. Massieu F (1869) Sur les fonctions caractéristiques des divers fluides. C R Acad Sci Paris 69(858–864):1057–1061
- 35. Maugin GA (1988) Continuum mechanics of electromagnetic solids. North-Holland, Amsterdam
- 36. Maugin GA (1992) Thermomechanics of plasticity and fracture. Cambridge University Press, U.K.
- 37. Maugin GA (1999) Thermodynamics of nonlinear irreversible behaviors. World Scientific, Singapore
- 38. Maugin GA, Muschik W (1994) Thermodynamics with internal variables. Part 1: General concepts, Part II. Applications. J Non-Equilibr Thermodynam 19: 217–249, 250–289
- 39. Maugin GA, Trimarco C (1994) Material Forces and Irreversible Progress of Thermoelastic Phase-transition Fronts. Euromech Colloquium on Phase Transitions in Solids in the Honour of J.L. Ericksen, Udine, May 1994 [Cf. Meccanica (Italy) 30: 605–619, 1995]
- 40. Maxwell JC (1873) A Treatise on Electricity and Magnetism. Clarendon Press, Oxford (Dover reprint, two volumes, New York, 1954)
- 41. Mayergoz I (1991) Mathematical models of hysteresis. Springer, New York
- 42. Miller DG (1970) Entry: ''Pierre-Maurice-Marie Duhem''. In: Dictionary of Scientific Biographies. Ed. C.C. Gillispie, Vol 3, pp 225–233, Charles Scribner's Sons, New York
- 43. O'Rahilly A (1931) Electromagnetics. London, (reprinted as Electromagnetic Theory, Two volumes, Dover, New York, 1965)
- 44. Poincaré H (1890) Electricité et optique, Two volumes. Paris [Lecture notes of the Physics Course at the Sorbonne in 1888, the year electromagnetic waves were experimentally discovered and their speed of propagation shown to be equal to that of light by H. Hertz]
- 45. Roy L (1923) L'électrodynamique des milieux isotropes en repos d'après Helmholtz et Duhem. Paris
- 46. Truesdell CA (1986) Rational thermodynamics (revised and enlarged edition). Springer, New York (original edition, McGraw Hill), New York, p 1969
- 47. Truesdell CA, Noll W (1965) The Nonlinear Field Theories of Mechanics. In: Handbuch der Physik, Bd.III/3, Ed. S. Flügge, Springer, Berlin
- 48. Visintin A (1991) Bibliography of hysteresis. Preprint, University of Trento, New Jersey