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BOOK REVIEW

# Unearthing a buried memory

## Stefano Bordoni: Taming complexity: Duhem's third pathway to thermodynamics. Urbino: Editrice Montefeltro, 2012, 288pp, €30.00 PB

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The third of a series of articles under the general title "Commentaires aux principles de la Thermodynamique" concludes with an expression of Duhem's third way of developing thermodynamics:

> The founders of thermodynamics have nearly all been inclined to make this science an application of dynamics. Regarding heat as a very small and rapid motion of the particles constituting a body, the temperature as the average living force of this motion, and changes of physical state as changes of characteristic elements of this motion, they have tried to deduce the theorems of thermodynamics from the theorems of rational mechanics. Their efforts were readily crowned with success in the domain of the principle of the conservation of energy. They were less successful when they grappled with Carnot's principle. … Many physicists have sought to render thermodynamics independent of all hypotheses about the nature of heat. They have tried to establish it, not on theorems obtained from rational mechanics, but on principles of its own. … We have tried in the present work to suggest a third position of dynamics … [making] dynamics a particular case of thermodynamics, or rather, we have constituted, under the name thermodynamics, a science which covers in shared principles all the changes of state of bodies, including both changes of position and changes in physical qualities. … We have put the equations of this science, first outlined by Clausius, and perfected by Massieu, Gibbs and Helmholtz, into an analytic form like that Lagrange gave to mechanics. A continuity of tradition is thus maintained in the course of the evolution of science which assures progress.
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> If the science of motion ceases to be the first of the physical Sciences in logical order, and becomes just a particular case of a more general science

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> including in its formulas all the changes of bodies, the temptation will be less, we think, to reduce all physical phenomena to the study of motion. … It will then be easier to get away from what has hitherto been the most dangerous stumbling block of theoretical physics, the search for a mechanical explanation of the Universe. (Duhem 1894, 284–285).

After an introductory chapter, Bordoni presents the first two of these pathways in Part I of his book and goes on to discuss Duhem's development of the third pathway in Part II. The details of Maxwell's and Boltzmann's contributions to statistical mechanics are reviewed in Chapters 2 and 3, where Planck's doubts are mentioned and the late nineteenth-century debate on the foundations of thermodynamics is taken up. The contributions of physicists and engineers, including Reech, Massieu, Rankine, Gibbs, Helmholtz and Planck, to the second pathway are reviewed in Chapters 4 and 5. The last hundred pages or so discuss Duhem's development of generalised thermodynamics or energetics into the realm of irreversible processes. Several of Duhem's contemporaries propounded programmes likewise called energetics but which were quite distinct from his. Ostwald's, in particular, "appears quite naïve when compared to Duhem's appreciation … [of] the structural analogies between different fields of science … [which] were the keystone to Duhem's design of unification, where Analytical Mechanics, Thermodynamics and Chemistry could find a natural re-interpretation" (199).[1]

These last hundred pages constitute Bordoni's distinctively new contribution to the literature on late nineteenth-century science relating to thermodynamics, in which he reviews Duhem's development of a unified formulation of mechanics and thermodynamics and its extensions to treat irreversible phenomena. It covers much the same ground as Bordoni (2012), but includes more detail.

Part II begins with a review, in Chapter 6, of the generalised thermodynamics in which Duhem recognises a deep conceptual link tying mechanics to thermodynamics despite the role of what Clausius called uncompensated work in the latter. Temperature and chemical composition are treated on a par with purely mechanical concepts of total mass, position, shape and velocity in the determination of the overall state of a system. Duhem thought of this as a generalisation of the notion of motion to accommodate change in qualities of bodies in addition to the mechanical ones relating to position in space. "[T]he word *motion* does not stand in opposition to the word *rest*, but to the word *equilibrium*" (Duhem 1894, 222). This Aristotelian analogy is strengthened in his study of chemical reactions subject to the dampening effect of a generalised viscosity. Although Duhem introduced this term on the strength of a structural analogy between chemistry and mechanics, the behaviour of a chemical system differs from that of a mechanical system when the viscosity vanishes. When mixtures like those of hydrogen and oxygen or hydrogen and chlorine are coaxed into reaction, so much heat is released as they transform into their true states of equilibrium that the process is explosive. The velocity of the chemical system becomes in effect infinite, as in Aristotle's theory of motion but unlike the situation in classical mechanics (232–233). This result arose as Duhem

[1] Ostwald's energetics is comprehensively discussed by Deltete (2007–2008).

pursued the implications of the uncompensated work involved in processes beyond the study of equilibrium characteristic of thermodynamics and into the realms of irreversible processes.

Duhem was virtually alone in attempting to "tame complexity", as Bordoni's title has it, in order to broach the real world of irreversible processes. Equations governing states of equilibrium were generalised with the introduction of new functions (of the same variables governing equilibrium states and their time derivatives) representing "*passive resistances* that the system has to overcome" (Duhem 1894, 223–224). Equilibrium was perturbed by friction-like forces executing a total work that can be expressed in terms of these functions. Unfortunately, the introduction of these functions yielded $n$ equations in $n + 1$ Lagrangian parameters, and Duhem had no mechanical generalisation for the temperature parameter, forcing him to look outside his formal structure to purely thermal processes for the missing equation giving temperature as a function of time (180). Laying down as a "fundamental hypothesis" that work done by the passive resistances is non-positive, Duhem was able to identify this work with Clausius' uncompensated work. This gave him a mechanical interpretation of the second law—not a microscopic mechanical explanation but "a macroscopic re-interpretation linked to a re-interpretation of the word "motion" in a new Aristotelian perspective" (182) in the spirit of his third way.

Duhem's theory of chemical reactions was not based on atomic ideas, which he argued were inessential to the understanding of structural formulas and related notions such as valency (185–186),[2] just as caloric was inessential to Lavoisier and Laplace's theory of heat (188). He sought to improve on earlier understanding of chemical reactions as exothermic or endothermic transformations, and in particular the role of temperature (187), in the light of the general puzzle that although equilibrium thermodynamics prescribed what transformations were possible, thermodynamically possible transformations sometimes do not actually occur. Under a certain temperature, for example, a mixture of hydrogen and oxygen will remain indefinitely a mixture although the matter is thermodynamically more stable when combined as water. Similarly for endothermic combinations: silver oxide does not decompose under 100 °C (210, fn. 2). Duhem coined the term *false equilibria* for apparently stable systems which should not, according to equilibrium thermodynamics, remain in equilibrium.

An earlier theory from 1893 enabled Duhem to explain why a bubble of steam cannot begin to grow inside a liquid, with the consequent delay in boiling, and similar delays in condensation and decomposition (213–214). But this was unsuitable for dealing with false equilibria, which he tackled by developing an analogy with mechanical friction. A body will not slide down an inclined plane as it should when subject only to gravity because the motion is opposed by a force of friction which has to be overcome. Analogously, a mixture of hydrogen and oxygen or a quantity of silver oxide is subject to a "viscosity" which has to be overwhelmed for the true equilibrium to be realised. Perhaps the effects of friction could be removed by polishing planes and choosing rigid bodies, but he doubted that his

[2] The relevant works are translated as Duhem (2000, 2002).

viscosity could be similarly eliminated entirely, and an intrinsic viscosity must be accommodated in the fundamental equations (215). Nevertheless, increase in temperature plays the same role in chemistry that increased smoothness plays in mechanics (227).

Duhem considered how a parameter, $\alpha$, defining the degree dissociation of a compound into its constitutive elements, varies with temperature (as abscissa) for systems at constant volume and at constant pressure. On either side of a curve tracing the true equilibrium are curves $ff'$ and $FF'$ enclosing a surrounding region of false equilibrium. In the case of exothermic compounds, the region below that of false equilibrium bounded by curve $ff'$ is "the seat of combination" and the region above that of false equilibrium bounded by curve $FF'$ is "the seat of dissociation" (228). For endothermic compounds, the region of dissociation bounded by curve $FF'$ is below that of false equilibrium, and the region of combination bounded by curve $ff'$ lies above the curve of true equilibrium. The exact shape of curves $ff'$ and $FF'$ could not be derived from Duhem's theory, but had to be determined by experiment. Depending on the initial value of $\alpha$, increasing the temperature leads to different final states of the system. "The previous history of the physical system influenced the result of the transformation" (288). An exothermic system initially containing no compound ($\alpha = 0$) and raised to a temperature $T$ produces a certain proportion, $\alpha_1$, of the compound corresponding to the point on curve $ff'$ where the temperature is $T$, whereas if the system initially comprises just the compound ($\alpha = 1$), heating to the same temperature results in dissociation when the proportion of the compound corresponds to a point, $\alpha_2$, on curve $FF'$ at temperature $T$, and $\alpha_2 > \alpha_1$. With the aid of simplifying assumptions, Duhem derived expressions for the velocity, $d\alpha/dt$, of chemical reactions which showed that increasing temperature smoothed dissipative effects (231) and, as already mentioned, in the limit of zero viscosity, the velocity becomes infinite.

Whereas Galileo gave birth to modern mechanics by ignoring friction, Duhem was attempting to restore to science the complexity of the real world (227). Despite Prigogine's, Miller's and Truesdell's acknowledgements of this work, it has been largely forgotten. Uffink (2001) omitted any mention of Duhem's contribution to the clarification of thermodynamic concepts. Although historians and philosophers have recognised Duhem's contribution to their fields, they have done little to connect it with his technical work. Bordoni therefore found himself "unearthing a buried memory", as he puts it in the title of the Afterword. In so doing, he has done a great service to Duhem scholarship.

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