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in the late XIX century**



# *Looking for a Rational Thermodynamics in the late XIX century\**

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ABSTRACT. From Rudolf Clausius' classical version of Thermodynamics two different traditions of research really emerged. If James C. Maxwell and Ludwig Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, others relied on a macroscopic and more abstract approach, which set aside specific mechanical models. Starting from 1869, the French engineer François Massieu was able to demonstrate that thermodynamics could be based on two "characteristic functions" or potentials. Josiah W. Gibbs and Hermann von Helmholtz exploited the structural analogy between Mechanics and Thermodynamics: from a mathematical point of view, Helmholtz's "free energy" was nothing else but Gibb's first potential. In the meantime, in 1880, the young German physicist Max Planck aimed at filling the gap between thermodynamics and the theory of elasticity. Five years later Arthur von Oettingen put forward a formal theory, where mechanical work and fluxes of heat represented the starting point of a dual mathematical structure. In 1891 Pierre Duhem generalized the concept of "virtual work" under the action of "external actions" by taking into account both mechanical and thermal actions. Between 1892 and 1894 his design of a generalized Mechanics based on thermodynamics was further developed: ordinary mechanics was looked upon as a specific instance of a more general science.

KEY WORDS: Mechanics, Thermodynamics, Potentials, Work, Heat, Energy, Lagrange's equations, General equations.

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## Introduction

In the 1860s and 1870s, the recently emerged Thermodynamics branched out into two different directions: the refinement of the kinetic theory of gases, and the questionable alliance between mechanical laws and statistical procedures, on the one hand, and the attempt at recasting Thermodynamics in accordance with the mathematical structures of Analytical Mechanics, on the other.

Starting from Joseph-Louis Lagrange, and in particular from his *Mécanique Analytique* (1788), Mechanics had undergone a meaningful generalisation, and an abstract physical space had replaced the ordinary Euclidean space in the tradition of mathematical physics. In the 1830s William Rowan Hamilton had put forward a very abstract Mechanics which was based on a set of variational Principles: dynamical entities could be chosen as physical co-ordinates. In 1839, an Irish mathematician and natural philosopher, James MacCullagh, on the same path as of Lagrange, had developed a mathematical theory of optics. On the same track, another Irish physicist, George Francis FitzGerald, put forward a Lagrangian theory of electromagnetic fields in 1880.<sup>1</sup>

In the last decades of the XIX century, electromagnetic theories had already been translated into fruitful technologies, which were deeply transforming the way of life of western people. The new age of electromagnetism, whose symbolic device was the electromagnetic transformer, seemed to supplant, at least in part, the old age of smoky thermal engines. Thermodynamics was not able to offer new technologies, but the new theoretical horizon opened by Clausius' second Principle led to three main results: a widespread philosophical and cosmological debate, the development of thermo-chemistry, and the mathematisation of the discipline.<sup>2</sup> Different theoretical pathways were undertaken by physicists, even though we can single out two main conceptual streams. If Maxwell and Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases, others relied on a macroscopic approach in term of continuous variables, which set aside specific mechanical models.<sup>3</sup> This approach was developed in different countries of Europe and the United States, in the course of about two decades. François Massieu, Josiah Willard Gibbs, Hermann von Helmholtz, and then Pierre Duhem, explored the connections between the specific contents of thermodynamics and the formal structures of Analytical Mechanics. Others, like the young Max Planck and the less young Arthur von Oettingen, pursued a sort of formal symmetry between thermal and mechanical variables.

Different *mechanical* theories of heat were on the stage in the last decades of the nineteenth century, and different meanings of the adjective *mechanical* were at stake. I would like to analyse and briefly discuss the second approach to Thermodynamics, and in particular its roots in Clausius and Rankine's researches around the middle of the XIX century, the developments which took place in the 1870s and 1880s, and finally Duhem's design of a very

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<sup>1</sup> For the primary sources see Hamilton W.R. 1834, MacCullagh J. 1848 (read 9 Dic. 1839), and FitzGerald G.F. 1880. On Hamilton's equations see Hankins T.L. 1980, pp. xv-xviii, 61-87, and 172-209. On MacCullagh's Lagrangian approach to Optics, and "Fitzgerald's electromagnetic interpretation of MacCullagh's ether", see Darrigol O. 2010, pp. 145-54, and 157-9.

<sup>2</sup> For the methodological and philosophical debated which stemmed from the second principle of Thermodynamics, see Kragh H. 2008, chapters 3 and 4.

<sup>3</sup> On Maxwell and Boltzmann's theories see Maxwell J.C. 1860, Maxwell J.C. 1867, Boltzmann L. 1872, and Boltzmann L. 1877.

general theory which stemmed from the formal unification between Mechanics and Thermodynamics. From the outset I would like to highlight one of the hallmarks of that tradition of research: the assumption of a new *physical space*, where thermal variables (and variables of other kind) merged with time and geometrical variables in order to describe complex physical events.

## 1. Mechanical models

In 1860 James Clerk Maxwell, then professor of Natural Philosophy at Marischal College in Aberdeen, published the paper “Illustration of the Dynamical Theory of Gases” in the *Philosophical Magazine*, a scientific journal which had already hosted dynamical theories of matter and heat. The starting point was the basic assumption of every kinetic theory of heat: matter consists of a huge number of microscopic particles.<sup>4</sup>

After having analysed a collision between two spheres “moving in opposite direction with velocities inversely as their masses”, Maxwell inquired into the effect of many collisions on the distribution of *vis viva* among the particles of a gas. He was looking for “some regular law”, allowing him to compute “the average number of particles whose velocity lies between certain limits”. He defined a function  $f(x)$  such that  $N f(x) dx$  was the number of particles whose velocity lay between  $x$  and  $x+dx$ , where  $f(x)$  was the fraction of such particles,  $N$  the total number of particles, and  $x, y, z$  the Cartesian components of particle velocity. He thought that “the existence of the velocity  $x$  does not in any way affect that of the velocities  $y$  or  $z$ ”, since the three components are “all at right angles to each other and independent”. According to that hypothesis, Maxwell wrote down the number of particles in a gas whose velocity “lies between  $x$  and  $x+dx$ , and also between  $y$  and  $y+dy$ , and also between  $z$  and  $z+dz$ :

$$N f(x) f(y) f(z) dx dy dz.^5$$

Another simplification arose from the rotational symmetry in the space of velocities: the law of the distribution of velocities had to be insensitive to the direction of velocities .

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x) f(y) f(z) = \phi(x^2 + y^2 + z^2)$$

Solving this functional equation, we find

$$f(x) = C e^{Ax^2}, \quad \phi(r^2) = C^3 e^{Ar^2} .^6$$

The constant  $A$  had to be negative, otherwise the number of particles with a given velocity would dramatically increase with the value of velocity, and the integration over the whole

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<sup>4</sup> On the relationship between the kinetic theory of gases and existing atomic models, see Brush S.G. 1976, book 1, p. 204: “Although the identification of heat with molecular motion was fairly widely accepted after 1850, many scientists continued to pursue molecular theories which they considered in some way superior to the kinetic theory, though not necessarily denying its applicability for some purposes. The two principal alternatives were the “dynamic” view of the atom as a centre of force, and the “atmospheric atom” which exchanged heat vibrations with other atoms through an intermediate ether; while these represented opposing world views, they were often mixed together.”

<sup>5</sup> Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 380. The mutual independence among the components does not hold good: the conservation of momentum and energy does not allow us to choose any value of  $y$  and  $z$  components for whatever choice of  $x$  component. See Brush S.G. 1976, book 2, pp. 587-8.

<sup>6</sup> Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 381.

range of velocities would dramatically diverge. After a simple procedure of normalisation, Maxwell obtained

$$f(x) = \frac{1}{\alpha\sqrt{\pi}} e^{-\frac{x^2}{\alpha^2}}.$$

The mathematical law for the distribution of velocities in a gas would therefore be nothing else but the statistical law of distribution of casual *errors* in every physical process of measurement.

It appears from this proposition that the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the ‘method of least squares’. The velocities range from 0 to  $\infty$ , but the numbers of those having great velocities is comparatively small.<sup>7</sup>

After seven years, Maxwell published a more massive and demanding paper, “On the Dynamical Theory of Gases”, in the *Philosophical Transaction*, the official review of the Royal Society.<sup>8</sup> The title of the second section, “On the Final Distribution of Velocity among the Molecules of Two Systems acting on one another according to any Law of Force”, seems misleading, since no law of force was involved in the determination of the distribution. He explicitly confined himself to a globally constant distribution over time, wherein “the number of molecules whose velocity lies within given limits remains constant”. If  $a$  and  $b$  were the velocities of two molecules of different kind before the collision,  $a'$  and  $b'$  the velocities after the collision, and  $f(v)$  the required distribution of velocities, then the number of molecules of the first and second kind should have been

$$n_1 = f_1(a)dV, \quad n_2 = f_2(b)dV,$$

where  $dV$  was an element of volume.<sup>9</sup>

The key passage consisted of two steps. First, Maxwell assumed that “the number of encounters of the given kind between these two sets of molecules” was proportional to  $f_1(a)f_2(b)$ . Then he assumed that “the number of pairs of molecules which change their velocities” from  $a$  and  $b$  to  $a'$  and  $b'$  was “equal” to the number of couples (or collisions) wherein velocities were transformed from  $a'$  and  $b'$  into  $a$  and  $b$ . The first step corresponded to a hypothesis of independence between physical events: the members of a couple had no correlation. Molecules were looked upon as free particles: they had neither interactions nor history. This sounds quite strange from the physical point of view: collisions are ruled by

<sup>7</sup> Maxwell J.C. 1860, in Maxwell J.C. 1890, vol. 1, p 381.

<sup>8</sup> In 1860 Maxwell had been appointed to the chair of Natural Philosophy at King’s College in London, but in 1865 he left London and returned to his Scottish estate.

<sup>9</sup> Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 43-4.

physical laws, and moreover a definite law of force had been assumed by Maxwell himself. In other words, the statistical approach looks upon molecules and collisions as sets of casual events.<sup>10</sup>

The second step corresponded to a hypothesis of uniformity or equalisation over time: the fluctuations in the distribution of velocities were assumed to preserve the state of equilibrium. In some way, the equilibrium was assumed rather than deduced from the theory. The corresponding relationship,

$$f_1(a)f_2(b) = f_1(a')f_2(b'),$$

together with the principle of conservation of energy,

$$M_1 a^2 + M_2 b^2 = M_1 a'^2 + M_2 b'^2$$

led to distributions of the form

$$f_1(a) = C_1 e^{-\frac{a^2}{\alpha^2}} \quad \text{and} \quad f_2(b) = C_2 e^{-\frac{b^2}{\beta^2}},$$

where  $M_1 \alpha^2 = M_2 \beta^2$ .

Therefore, “the number of molecules whose component velocities are between”  $\xi_1$  and  $\xi_1 + d\xi_1$ , ...  $[\xi_1; \xi_1 + d\xi_1]$ ,  $[\eta_1; \eta_1 + d\eta_1]$  and  $[\zeta_1; \zeta_1 + d\zeta_1]$  was

$$dN_1 = \frac{N_1}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi d\eta d\zeta. \quad ^{11}$$

Even though Maxwell’s 1867 deduction of the law of distribution is different from his 1860 deduction, it makes reference to the same probabilistic law: the product of probabilities for independent events. As already remarked, he assumed the mutual independence between  $n_1$  and  $n_2$ , namely the absence of whatsoever dynamical correlation between the molecules with velocity  $a$  and the molecules with velocity  $b$ . It seems that Maxwell firmly believed in the necessity of a distribution of the kind *distribution of errors*, pivoted around its average value, and was looking for the best way to deduce it. When he got rid of his 1860 deduction while

<sup>10</sup> On the difference between the conditions of independence in Maxwell’s 1860 and 1867 papers, see Brush S. 1976, book 2, pp. 587-8.

<sup>11</sup> Maxwell J.C. 1867, in Maxwell J.C. 1890, vol. 2, pp. 44-5. Obviously, the hypothesis of statistical independence could not be applied to molecules emerging from a collision. See Cercignani C. 1997, p. 69.



preserving the same result, no experiment suggested one law of distribution rather than another: he expected a Gaussian law of distribution only on theoretical grounds. The motion of molecules appears locally predictable, and ruled by definite laws of motion, but globally unpredictable, even though it led to a distribution statistically uniform over time.<sup>12</sup>

In the 1870s, the Austrian physicist Ludwig Boltzmann tried to go far beyond Maxwell's microscopic interpretation of equilibrium in rarefied gases: he aimed at inquiring into the processes leading to equilibrium. In the first lines of his 1872 paper "Weiteren Studien über das Wärme Gleichgewicht unter Gasmolekülen", he reminded the reader about the foundations of the mechanical theory of heat. Molecules were always in motion, but the motion was invisible and undetectable: only the "average values" could be detected by human senses. Those microscopic undetectable motions gave rise to "well-defined laws" at the macroscopic level, which involved the observed average values.<sup>13</sup>

A thermodynamic theory required therefore two different levels: a microscopic invisible, and a macroscopic visible one. Statistics and probability could bridge the gap between the two levels. Just at the end of the first page, Boltzmann sharply stated that "[p]roblems emerging from the mechanical theory of heat are probabilistic problems". He claimed that probability did not mean uncertainty: the presence of the laws of probability in the mechanical theory of heat did not represent a flaw in the foundations of the theory. Probabilistic laws were ordinary mathematical laws as certain as the other mathematical laws: we should not confuse an "incomplete demonstration" with a "completely demonstrated law of the theory of probability".<sup>14</sup>

The pivotal mathematical entity was "the number of molecules whose living force lies between  $x$  and  $x + dx$ , at a given time  $t$ , in a given space  $r$ ": Boltzmann labelled  $f(x,t)dx$  this differential function. From the mathematical point of view, he had to face a "two-steps task": the "determination of a differential equation for  $f(x,t)$ ", and the subsequent "integration". He assumed that "the variation of the function stemmed only from the collisions" between couples of molecules. The keystone of the whole procedure was therefore the computation of the collisions. The function  $f(x,t)$  did not belong to the tradition of mathematical physics: a re-interpretation of the concepts of dynamic equation and time-

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<sup>12</sup> Maxwell devoted two papers to gas theory after 1867. Brush, Everitt and Garber remarked that, in the end, "gas theory and electromagnetic theory underwent in Maxwell's hands closely similar developments from the use of a specific model to the successive reformulation of the original ideas in more and more abstract terms". (See Brush S., Everitt C.W.F. and Garber E. 1986b, pp. xvii and xxiii) Although the authors stated that "[t]he attempt with electromagnetic fields was more successful because all known phenomena could be brought within the formulation", Maxwell's more abstract (Lagrangian) approach to electromagnetic phenomena was not so general as the authors claimed. See Stein H. 1981, pp. 311-2, and D'Agostino S. 2000, p. 117.

<sup>13</sup> Boltzmann L. 1872, in Boltzmann L. 1909, I Band, p. 316. The expression *Wiener Berichte* is usually used as a short form for the complete name of the Austrian journal where he published important contributions to Thermodynamics: "Sitzungsberichte der kaiserlichen Akademie der Wissenschaften – mathematisch-naturwissenschaftliche Classe". At the time Boltzmann held the chair of theoretical physics in Graz, and had already published some papers on different subjects. His scientific career began with researches on electricity, in particular the relationship between electromagnetism and optics. Together with other German-speaking physicists (August Föppl for instance), he then introduced Maxwell's electromagnetic theory to the Continental scientific community. See Dugas R. 1959, p. 135, Brush 1976, book 1, p. 244, and Buchwald J.Z. 1985, pp. 189 and 197.

<sup>14</sup> Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 317-8.

evolution of a physical system was at stake. That function had to bridge the gap between two different traditions in Mechanics: the laws of scattering between solid bodies, which were confined at the invisible microscopic level of interacting molecules, and the equations of motions, which ruled the macroscopic observable behaviour of the whole gas. Boltzmann demonstrated that the “fundamental equation for the variation of the function  $f(x,t)$ ” had the following structure:

$$\frac{\partial f(x,t)}{\partial t} = \int_0^{x+x'} \int_0^x \left[ \frac{f(\xi,t)}{\sqrt{\xi}} \frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}} - \frac{f(x,t)}{\sqrt{x}} \frac{f(x',t)}{\sqrt{x'}} \right] \cdot \sqrt{x x'} \psi(x,x',\xi) dx' d\xi.$$

Immediately he remarked that the stationary function  $f(x,t) = f(x) = C\sqrt{x} e^{-hx}$ , which was nothing else but Maxwell distribution of velocities, made  $\partial f(x,t)/\partial t$  vanish in the above equation.<sup>15</sup>

Boltzmann aimed at a generalisation of Maxwell’s results: he focussed on another function  $E$  generated by  $f(x,t)$ , and on its time derivative:

$$\begin{aligned} E &= \int_0^{\infty} f(x,t) \left\{ \log \left[ \frac{f(x,t)}{\sqrt{x}} - 1 \right] \right\} dx. \\ \frac{dE}{dt} &= \int_0^{\infty} \left\{ \frac{\partial f(x,t)}{\partial t} \left[ \log \left( \frac{f(x,t)}{\sqrt{x}} - 1 \right) \right] + f(x,t) \left[ \frac{\sqrt{x}}{f(x,t)} \frac{1}{\sqrt{x}} \frac{\partial f(x,t)}{\partial t} \right] \right\} dx. \\ &= \int_0^{\infty} \left\{ \frac{\partial f(x,t)}{\partial t} \left[ \log \left( \frac{f(x,t)}{\sqrt{x}} - 1 \right) \right] + \frac{\partial f(x,t)}{\partial t} \right\} dx = \int_0^{\infty} \frac{\partial f(x,t)}{\partial t} \log \left( \frac{f(x,t)}{\sqrt{x}} \right) dx. \end{aligned}$$

After a long and demanding computation, he showed that “ $E$  must necessarily decrease”, and he expected that it approached a minimum value, which corresponded to  $dE/dt = 0$ . This is a very sensitive issue, because the decrease of a function does not assure the existence of a minimum value. Only in this specific case,  $df/dt = 0$ , which was satisfied for every stationary function of the kind

$$f(x,t) = f(x) = C\sqrt{x} e^{-hx}.^{16}$$

Boltzmann thought that the mathematical result had a deep meaning in the context of the kinetic theory and Thermodynamics:  $dE/dt$  could be associated to the integral  $\int dQ/T$ , which “is in general negative, and vanishes in the limiting case of a reversible cyclic process”.

<sup>15</sup> Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 322 and 332-4.

<sup>16</sup> Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 335 and 344-5.

It seemed to Boltzmann that his interpretation of the second Principle was more general than previous interpretations. In particular, it could account for irreversible processes, just the kind of processes “really taking place in nature”, whereas the reversible ones were “purely ideal”.<sup>17</sup>

In 1877 he published an even longer paper, where he reminded the reader that the function  $E$  he had introduced in 1872 could never increase, and that it reached its minimum value at thermal equilibrium. His physical model of gas was not so far from the model he had put forward five years before. The gas was “contained in a vessel with rigid and elastic walls”, and the molecules interacted as they were equally rigid and elastic balls. Another suitable model was that of “centres of force” endowed with a specific law of force: only when their distances became “less than a given value”, they experienced some kind of interaction. This allowed Boltzmann to combine two different processes, which stemmed from two different mechanical traditions: the continuity of unperturbed trajectories, and the discontinuity of sudden collisions.<sup>18</sup>

The molecules could assume only discrete values of velocity: the model was qualified by Boltzmann himself as “fictitious” and “not corresponding to an actual mechanical problem”, although “much easier to handle mathematically”. The series of available “living forces” corresponded to an “arithmetic progression”  $0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots, p\varepsilon$  with an upper bound  $P = p\varepsilon$ . These values of the energy could be “distributed over the  $n$  molecule in all possible ways”, provided that the sum of all energies was preserved over time, and assumed a given value  $\lambda \cdot \varepsilon = L$ .<sup>19</sup>

He re-defined “the measure of the permutability” in a slightly different way,

$$\Omega = - \int \int \int \int f(x,y,z;u,v,w) \ln[f(x,y,z;u,v,w)] dx dy dz du dv dw ,$$

where  $x,y,z$  were spatial coordinates and  $u,v,w$  velocity coordinates. The integral was extended to a six-dimensional hyper-space, and the minus before the integral transformed the search for the minimum into the search for the maximum. This was the quantity whose value had to be computed “when the gas has reached thermal equilibrium”. As already shown, at the equilibrium,

$$f(x,y,z;u,v,w) = \frac{N}{V \left( \frac{4\pi T}{3m} \right)^{3/2}} e^{-\frac{3m}{4T}(u^2 + v^2 + w^2)},$$

<sup>17</sup> Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 345-6.

<sup>18</sup> Boltzmann L. 1877, in Boltzmann L. 1909, II Band, p. 166. Dugas reminded us that Boltzmann’s theoretical representation of atoms and molecules evolved over time. In the first volume of his *Vorlesungen über Gastheorie* (1895-1898), we find molecules as “elastic spheres” and then molecules as “centres of force”, whereas in the second volume, molecules are represented as “mechanical systems characterized by generalized coordinates”. See Dugas R. 1959, pp. 25 and 79, footnote 5 included.

<sup>19</sup> Boltzmann L. 1877, in Boltzmann L. 1909, II Band, pp. 167-9.

where  $V$  was the volume of the gas,  $m$  the mass of every molecule,  $T$  the average living force, and  $N$  the number of molecules. When we put the function into  $\Omega$ , the integral yields

$$\Omega = N \log \left[ V \left( \frac{4\pi T}{3m} \right)^{3/2} \right] + \frac{3}{2} N - N \ln N. \text{ }^{20}$$

Apart from the reversed signs and the last constant on the right-hand side, Boltzmann arrived essentially at the expression already found in 1872, but in this case he tried to carefully compute the entropy, starting from a particular expression of the first Principle, and the equation of state for perfect gases:

$$dQ = NdT + pdV, \quad pV = \frac{2}{3} NT.$$

The computation of entropy required only some simple steps, and it led to

$$\int \frac{dQ}{T} = \int N \frac{dT}{T} + \int \frac{pdV}{T} = N \ln T + C_1 + \int \frac{2}{3} \frac{NT}{VT} dV = \frac{2}{3} N \ln(VT^{3/2}) + C.$$

Once again Boltzmann stressed the structural similarity between the function  $\Omega$ , representing the probability of a given state, and the entropy  $dQ/T$  in any “reversible change of state”.<sup>21</sup>

In reality, in the 1880s, on the European Continent, some scientists cast doubts on atomism and microscopic interpretations of the second principle of Thermodynamics: they pursued a phenomenological and macroscopic approach, which set aside specific mechanical models. In 1893, Poincaré remarked that Mechanics required that “all phenomena are *reversible*”, even though every experience contrasted that requirement: thermal conduction was a well-known instance of irreversibility. That a scientist could expect thermal irreversibility to stem from the laws of Mechanics, seemed logically inconsistent to Poincaré: how could we rely on a theory wherein “we find reversibility at the outset, and irreversibility at the end”?<sup>22</sup>

<sup>20</sup> Boltzmann L. 1877, in Boltzmann L. 1909, II Band, pp. 215-6. The general solution of the integral-differential equation for  $f(x,t)$  was found in 1916-7. See Brush 1976, book 1, p. 237, and book 2, p. 449.

<sup>21</sup> Boltzmann L. 1877, in Boltzmann L. 1909, II Band, pp. 216-7. For a comparison with his 1872 line of reasoning, see Boltzmann L. 1872, in Boltzmann L. 1909, I Band, pp. 399-400. Cassirer found that Boltzmann had managed to remove the “paradoxical and extraneous nature (Fremdheit)” of the second Principle of Thermodynamics in the context of Mechanics. Just for this reason, he qualified Boltzmann as “one of the most rigorous representatives of classic Mechanics”. See Cassirer E. 1936, pp. 95-6. The fact is that, in Boltzmann’s theory, the second Principle did not stem from Mechanics, but from statistical and probabilistic hypotheses unrelated to Mechanics. Just for this reason, I find that Boltzmann was not a “classical physicist”.

<sup>22</sup> Poincaré H. 1893, pp. 534-7. In 1896 and 1897 Boltzmann answered systematically to Zermelo and Poincaré’s criticism, and stressed the intrinsic statistical nature of his approach: from his point of view, “Poincaré’s theorem”

In 1894, Boltzmann took part to the annual meeting of the British Association for the Advancement of Science, and his communications raised some debate, which continued in the pages of the scientific journal *Nature* in 1895. The British physicists Edward P. Culverwell, Joseph Larmor, Samuel H. Burbury, George H. Bryan, and Henry W. Watson's discussed and criticised Boltzmann's theory. The British journal also hosted a paper where Boltzmann tried to clarify his probabilistic approach to Thermodynamics.<sup>23</sup>

However, in the second half of the nineteenth century, a different pathway to Thermodynamics was undertaken by engineers who were familiar with abstract generalisations and Analytical Mechanics. The most important difference between this pathway and Maxwell and Boltzmann's pathway dealt with the relationship between Thermodynamics and Mechanics. According to the former, a general mathematical framework had to be set up, without any reference to microscopic structure underlying the physical system under consideration. According to the latter, microscopic mechanical models, mixed with extra-mechanical hypothesis of probabilistic nature, were expected to account for the thermodynamic behaviour of macroscopic systems. Expressions like "mechanical theory of heat" had different meanings when interpreted in the two different perspectives: formal similarities between the mathematical structures of Thermodynamics and Mechanics in the first case, and specific mechanical models in the second.

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was "completely in accordance" with his own theorems. In 1896 he remarked that the entity of Poincaré's recurrence time "makes a mockery of every attempt at observing it", and in 1897 stressed that "[i]n practice ... a numerical upper boundary for the time of recurrence ... cannot be specified". See Boltzmann L. 1896, in Boltzmann L. 1909, III Band, p. 571, and Boltzmann L. 1897, in Boltzmann L. 1909, III Band, p. 595. For the debate, see Dugas R. 1959, pp. 207-8 and 212-3, Brush S. 1976, book 1, p. 96, and Brush S. 1976, book 2, pp. 356-63. In 1906 Poincaré returned to the concept of entropy, and put forward two different kinds of entropy. See Cercignani C. 1997, pp. 98-9, 103, and 149.

<sup>23</sup> See, for instance, Culverwell E.P. 1895, p. 246, and Boltzmann L. 1895, in Boltzmann L. 1909, III. Band, p. 535. See also Brush S. G. 1976, book 2, p. 622.

## 2. The roots of a formal analogy

In 1854 Clausius stated that the equivalence between heat and work, and “Carnot’s proposition” did not necessarily clash, provided that the latter was slightly modified. To the above law of equivalence he associated another law of equivalence, in order to maintain a sort of symmetry in the axiomatic structure of Thermodynamics: a law of equivalence between “transformations”. He specified that two kinds of transformations were at stake in thermal machines: the transformation of heat into work, and the transformation of an amount of heat, which was stored in the boiler at a high temperature, into heat which is received by the cooler at a low temperature. Clausius pointed out that the two kinds of transformation were tightly linked to each other: the former could not take place without the latter.<sup>24</sup>

The second law became a law of equivalence between “transformations”, in order to maintain a sort of symmetry in the axiomatic structure of Thermodynamics. This formulation of the second law, pivoted on the concept of “equivalence value”  $Q/T$ , where  $T$  was a function of temperature. From the linguistic and conceptual points of view, the two laws of Thermodynamics were nothing else but two principles of equivalence: if the first stated the equivalence between heat and work, the second stated the equivalence between mathematically well-defined values of “transformation”.<sup>25</sup>

He assumed the transformation of work into heat as a positive quantity, and the transfer of heat from a high to a low temperature equally positive. In the case of  $K_1, K_2, \dots, K_n$  bodies, to be found at the temperatures  $t_1, t_2, \dots, t_n$ , he assumed that the quantities  $Q_1, Q_2, \dots, Q_n$  of exchanged heat were positive when received, and negative when sent off. Then he defined a quantity  $N$  as the sum of all “the values of transformation”

$$N = \sum \frac{Q}{T}.$$

In general, when temperatures changed in the course of every transformation, the sum had to be replaced by the integral

$$N = \int \frac{dQ}{T}.$$

In the case of “reversible cyclic processes”, the sum or the integral vanishes ( $\oint dQ/T = 0$ ), as required by a law of conservation: the sum of all contribution along a closed path must necessarily vanish.<sup>26</sup>

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<sup>24</sup> Clausius R. 1854, in Clausius R. 1864, p. 133: “*In allen Fällen, wo eine Wärmemenge in Arbeit verwandelt wird, und der diese Verwandlung vermittelnde Körper sich schliesslich wieder in seinem Anfangszustande befindet, muss zugleich eine andere Wärmemenge aus einem wärmeren in einem kälteren Körper übergehen, und die Grösse der letzteren Wärmemenge im Verhältnis zur ersteren ist nur von den Temperaturen der beiden Körper, zwischen welchen sie übergeht, und nicht von der Art des vermittelnden Körpers abhängig*”. See also pp. 127-8.

<sup>25</sup> Clausius R. 1854, in Clausius R. 1864, p. 143.

<sup>26</sup> Clausius R. 1854, in Clausius R. 1864, pp. 140, 144-5, and 147.

A formal analogy between Mechanics and Thermodynamics was thus established. The sum of “the contents of transformation (Verwandlungsinhalt)” had to vanish in pure, “reversible (umkehrbar)” thermodynamic processes, as well as the sum of mechanical works along a closed path had to vanish in pure mechanics, wherein dissipative effects were neglected. When the processes were irreversible, there was a loss of “Verwandlungsinhalt”, and the above integral became positive: the initial conditions could not be restored, and the transformation was “uncompensated”.<sup>27</sup>

The tradition of mechanics also offered structural analogies to Rankine: the whole of physics could be unified by the generalisation of the concepts of “*Substance*”, “*Mass*”, “*Work*”, and energy. He insisted that such terms had to be looked upon as “purely abstract” or as “names” which made reference to “very comprehensive classes of objects and phenomena”, rather than associated to “any particular object” or “any particular phenomena”. He attained a further generalisation by introducing the terms “*Accident*” and “*Effort*”. If the former could be identified with “every variable state of substances”, the latter was a generalisation of the concepts of force and pressure. The concept of “*Passive Accident*” was not fundamentally different from the concept of accident, apart from the further qualification of “condition which an effort tends to vary”. It had to be distinguished by the concept of “*Complex Accident*”, which corresponded to “the whole condition or state of a substance”: for instance, “thermic condition of an elastic fluid”, and “condition of strain ... in an elastic solid” were complex accidents for they required more than one independent variable (accident) to be specified.<sup>28</sup>

The concept of work encompassed *accidents* and *efforts*, and was a key concept in Rankine’s theory. The new meaning of the word “work” stemmed from the generalisation of the meaning of the words *force* and *displacement*, which corresponded to the new words *effort* and *accident*. The generalisation of the concept of work entailed the generalisation of the concept of energy, which was the core of Rankine’s *Energetics*. The concept of “*Actual energy*” was a generalisation of the mechanical *living force*: it included “heat, light, electric current”, and so on. The concept of “*Potential energy*” was extended far beyond gravitation, elasticity, electricity and magnetism. It included “chemical affinity of uncombined elements”, and “mutual actions of bodies, and parts of bodies”. In general, work was the result of “the variation of any number of independent accident, each by the corresponding effect”:

$$W = X dx + Y dy + Z dz + \dots\dots^{29}$$

Rankine’s theoretical design required the re-interpretation of thermodynamic transformations in terms of transformations of actual energy, and then a further generalisation, in order to extend that re-interpretation to all physical sciences.<sup>30</sup>

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<sup>27</sup> See Clausius R. 1854, in Clausius R. 1864, pp. 151-2: “Wir werden uns nun zur Betrachtung der nicht umkehrbaren Kreisprocesse. [...] Die algebraische summe aller in einem Kreisprocesse vorkommenden Verwandlungen kann nur positiv sein. Wir wollen eine solche Verwandlung, welche am Schlusse eines Kreisprocesses ohne eine andere entgegengesetzte übrig bleibt, und welche nach diesem Satze nur positiv vorkommen kann, kurz eine uncompensirte Verwandlung nennen.”

<sup>28</sup> Rankine M. 1855, in Rankine M. 1881, pp. 214-6.

<sup>29</sup> Rankine M. 1855, in Rankine M. 1881, pp. 216-7 and 222.

From the outset, explicit meta-theoretical commitments emerge from Rankine's paper. He distinguished between two kinds of scientific practice: the "ABSTRACTIVE" and the "HYPOTHETICAL". In the former, scientists confined themselves to a mathematical re-interpretation and classification of physical phenomena; in the latter, they relied on models and analogies, in order to catch the intimate nature of phenomena or the hidden structures underlying them.<sup>31</sup>

Obviously, Rankine's reference to the possibility of practising science without making recourse to "anything hypothetical" is not consistent with whatever kind of actual scientific practice: it seems more an idealisation or a rhetorical contrivance than an actually pursued design. Nevertheless, the distinction put forward by Rankine was not meaningless, and his energetics was a sort of mathematical phenomenology interconnected with a strong commitment to theoretical unification. He did not distrust models and analogies in the strict sense, for he tried to extend the formal framework of mechanics to all physics. He distrusted too specific mechanical models, in particular their narrow scope.<sup>32</sup>

In reality, Rankine did not disdain mechanical models: in 1851 he had devoted a paper to the relationship between heat and centrifugal forces arising from microscopic vortices. In 1853, in the paper "On the Mechanical Action of Heat – Section VI", he had discussed the "supposition" of "molecular vortices", the hypothesis that "heat consists in the revolutions of what are called molecular vortices", and he had more specifically assumed that "the elasticity arising from heat is in fact centrifugal force".<sup>33</sup>

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<sup>30</sup> In his 1855 paper, the passages wherein he displayed his ambitious design are extremely synthetic. If we want to understand and appreciate the complex network of assumptions and derivations, we should first take a look at two papers he had read before the Philosophical Society of Glasgow in January 1853 ("On the Mechanical Action of Heat" and "On the General Law of the Transformation of Energy"), and then return to his 1855 paper.

<sup>31</sup> See Rankine M. 1855, in Rankine M. 1881, p. 210: "According to the ABSTRACTIVE method, a class of object or phenomena is defined by describing, or otherwise making to be understood, and assigning a name or symbol to, that assemblage of properties which is common to all the objects or phenomena composing the class, as perceived by the senses, without introducing anything hypothetical. According to the HYPOTHETICAL method, a class of object or phenomena is defined, according to a conjectural conception of their nature, as being constituted, in a manner not apparent to the senses, by a modification of some other class of objects or phenomena whose laws are already known. Should the consequences of such a hypothetical definition be found to be in accordance with the results of observation and experiment, it serves as the means of deducing the laws of one class of objects or phenomena from those of another."

<sup>32</sup> Rankine M. 1855, in Rankine M. 1881, pp. 210 and 213. It is worth noting that the distinction between *abstractive* and *hypothetical* theories was rephrased at the end of the century, in the context of the emerging theoretical physics (See the *Foreword* in the present book). Rankine's choice of labelling "*objective*" and "*subjective*" the two interpretations of the "hypothetical method" appears quite misleading.

<sup>33</sup> See Rankine M. 1853a, in Rankine M. 1881, p. 310. In his 1851 paper, he reminded the reader about a specific atomic model he had already outlined the year before. See Rankine 1851, in Rankine M. 1881, p. 49: "In that paper the bounding surfaces of atoms were defined to be imaginary surfaces, situated between and enveloping the atomic nuclei, and symmetrically placed with respect to them, and having this property – that at these surfaces the attractive and repulsive actions of the atomic nuclei and atmospheres upon each particle of the atomic atmosphere balance each other."



### 3. A family of Potentials

After fourteen years, a French engineer took the path of a mathematical generalisation of Thermodynamics. In two short papers published in the *Comptes Rendus*, François Massieu tried to dress Thermodynamics with the garments of a general mathematical theory. The infinitesimal amount of heat  $dQ$  received by a body could produce three effects: “external work” of dilatation, “internal work”, and an increase of body “sensible heat”. The last two effects could not be identified separately. From the mathematical point of view, at the microscopic level, a single function  $U$  accounted for the sum of “mechanical and thermal effects, which merge with each other”, in accordance with the principle of equivalence between heat and work”. The external work  $p dv$  was “thermally equivalent” to  $A p dv$ , wherein  $A$  was the well-known conversion factor between mechanical and thermal measures. The first principle could therefore be expressed by the equation

$$dQ = dU + A p dv.$$

If  $T$  was the “absolute temperature” ( $T = t + 273$ ), at the end of a “closed reversible cycle”, the result

$$\int \frac{dQ}{T} = 0$$

followed from “Joule and Carnot combined principles”. Therefore  $dQ/T$  was “the complete differential  $dS$  of a function  $S$  of the variables which are sufficient to define the state of the body”.<sup>34</sup>

After having chosen  $v$  and  $t$  (volume and temperature) as independent variables, and after some pages of derivations and other computations, he arrived at a function  $\psi$  whose differential

$$d\psi = \frac{U}{T^2} dt + \frac{A p}{T} dv$$

was a complete differential of the same variables. Massieu labelled “*characteristic function of the body*” the function  $\psi$ . The most important mathematical and physical step consisted in deriving “all body properties dealing with thermodynamics” from  $\psi$  and its derivatives. Not only could  $U$  and  $S$  be expressed in terms of the function  $\psi$ , but also  $\psi$  could be expressed in terms of  $U$  and  $S$ :

$$U = T^2 \frac{\partial \psi}{\partial t} \quad \text{and} \quad S = \psi + T \frac{\partial \psi}{\partial v}, \quad \text{or} \quad S = \frac{\partial}{\partial v} (T \psi) \quad \text{and} \quad \psi = S - \frac{U}{T}.^{35}$$

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<sup>34</sup> Massieu F. 1869a, p. 858. François Massieu was a mining engineer and professor at Rennes university.

Then Massieu introduced a second *characteristic function*  $\psi'$  in terms of the two variables  $t$  and  $p$ . He first defined a new function  $U' = U + A p v$ , and then put into operation the already mentioned and quite demanding mathematical engine. In the end,

$$U' = T^2 \frac{\partial \psi'}{\partial t} \quad \text{and} \quad S = \psi' + T \frac{\partial \psi'}{\partial t}, \quad \text{or} \quad S = \frac{\partial}{\partial t}(T \psi') \quad \text{and} \quad \psi' = S - \frac{U'}{T}.$$

In the case of ideal gases,

$$\frac{U'}{T} = \frac{U}{T} + \frac{A p v}{T} = \frac{U}{T} + \text{const},$$

and  $\psi$  and  $\psi'$  resulted the same function, apart from a constant value.<sup>36</sup>

Massieu claimed that not only could  $U$ ,  $p$ ,  $v$ ,  $Q$  and  $S$  be derived from  $\psi$  and  $\psi'$ , but also the specific heats at constant pressure or volume  $k$  and  $k'$ , and the coefficient of dilatation at constant pressure or volume  $\beta$  and  $\beta'$  could as well. Conversely he was able to give the specific mathematical expressions of  $\psi$  and  $\psi'$  in terms of  $T$ ,  $v$ ,  $p$ , and the specific heats  $k$  and  $k'$ , for ideal gases, saturated vapours and superheated vapours.<sup>37</sup>

After seven years, in an essay of almost one hundred pages published in the *Mémoires de l'Institut National de France*, he resumed the subject matter, and generalised and deepened his theoretical approach. Indeed, compared with the previous short paper, the essay had a wider scope, and exhibited an explicit meta-theoretical commitment. At first, he regretted “the poor connections among the different properties of bodies, and among the general laws of physics“. Nevertheless, according to Massieu, this gap had begun to be filled just by the unifying power of Thermodynamics, which he identified with “the mechanical theory of heat”.<sup>38</sup>

It is worth remarking that, in Massieu’s theoretical and meta-theoretical context, “mechanical” did not mean microscopic mechanical models in the sense of Maxwell and Boltzmann, but a mathematical approach on the track of Analytical Mechanics. According to Massieu, this “mechanical theory of heat” allowed mathematicians and engineer to “settle a link between similar properties of different bodies”. Thermodynamics could rely on a consistent set of general and specific laws, and his “characteristic functions” could be looked upon as the mathematical and conceptual link between general and specific laws.<sup>39</sup>

<sup>35</sup> Massieu F. 1869a, p. 859, and Massieu F. 1869b, p. 1058. In the first paper, Massieu did not distinguish partial from total derivatives.

<sup>36</sup> Massieu F. 1869b, pp. 1059-60.

<sup>37</sup> Massieu F. 1869b, pp. 1060-1.

<sup>38</sup> See Massieu F. 1876, p. 2: “En ce qui concerne les propriétés mécaniques et calorifiques des corps, la thermodynamique, ou théorie mécanique de la chaleur, a comblé la lacune. En effet, des deux principes généraux qui servent de base à cette science nouvelle découlent des relations qui n’avaient pu trouver antérieurement une expression nette et vraiment scientifique.”

<sup>39</sup> See Massieu F. 1876, pp. 2-3: “Les principes fondamentaux de la thermodynamique peuvent être représentés par deux équations générales applicables à toutes les substances; qu’on imagine, en outre, les formules ou

In this 1876 essay, the deduction of the characteristic function is shorter and simpler than in the previous paper. From  $dS = dQ/dT$  and  $dQ = dU + A p dv$ , we obtain  $T dS = dU + A p dv$ . The addition of the term  $S dt = S dT$  to both members yielded

$$T dS + S dT = dU + A p dv + S dT, \quad d(ST) = dU + A p dv + S dT,$$

$$d(ST - U) = A p dv + S dT.$$

Since the first member was a total differential, so was the second, and Massieu could write

$$dH = d(ST - U), \quad H = ST - U,$$

where the function  $H$  corresponded to the function  $\psi$  of the previous paper. Moreover

$$S = \frac{dH}{dt}, \quad A p = \frac{dH}{dv}, \quad U = ST - H \quad \text{or} \quad U = T \frac{dH}{dt} - H.^{40}$$

The choice of  $t$  and  $p$  instead of  $t$  and  $v$  as independent variables led to Massieu's second characteristic function  $H'$ , which corresponded to the function  $\psi'$  of the previous paper. A two-fold strategy, both mathematical and physical, was at stake. On the one hand, the knowledge of specific parameters and specific laws describing the physical system under consideration allowed the researcher to write explicit expression for  $U'$ ,  $Q$  and  $S$ , and then  $H'$ .

Ces formules pourront être d'un usage commode lorsque l'on connaîtra un corps par l'expression de sa chaleur spécifique  $k$  à pression constante, et par la loi qui lie son volume  $v$  à sa pression  $p$  et à sa température  $t$ ; elles permettront d'obtenir les expressions de  $S$  et de  $U'$ , et par suite l'expression de la fonction caractéristique  $H'$  de ce corps.<sup>41</sup>

On the other hand, all parameters and specific equations describing the specific system could be derived from the knowledge of  $H'$ : in Massieu's words, after having put the mathematical engine into operation, "it is only a matter of computation".

Lors donc qu'on voudra vérifier l'exactitude d'une loi, on l'exprimera au moyen de la fonction caractéristique; s'il s'agit d'une loi générale applicable à tous les corps, son expression devra se réduire à une identité; s'il s'agit d'une loi applicable seulement à une catégorie de corps

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équations spéciales qui expriment les diverses propriétés calorifiques et mécaniques d'un corps déterminé, telle que l'expérience peut les fournir directement, ces équations devront être compatibles avec les équations générales de la thermodynamique, dont on pourra alors faire usage pour réduire, par élimination, les formules relatives à chaque corps à un nombre moindre de relations. Je suis parvenu à effectuer cette élimination d'une façon entièrement générale, et je montre, dans ce mémoire, que toutes les propriétés d'un corps peuvent se déduire d'une fonction unique, que j'appelle la fonction caractéristique de ce corps, et dont je donne l'expression pour les divers fluides."

<sup>40</sup> Massieu F. 1876, pp. 9-10.

<sup>41</sup> Massieu F. 1876, p. 29.

caractérisés par certaines propriétés, l'expression de la loi devra encore se réduire à une identité lorsqu'on aura tenu compte de ces propriétés.<sup>42</sup>

An abstract approach and wide-scope generalisations were also the hallmarks of J. Willard Gibbs's researches on Thermodynamics.<sup>43</sup> In the first lines of his collection of papers, Gibbs stated that his theoretical approach was based on the two fundamental principles of Thermodynamics, which had been put forward by Clausius in 1865. Starting from two basic entities, energy and entropy, he would have set up "the laws which govern any material system": energy and entropy's "varying values" would "characterize in all that is essential" the transformations of every system. His theoretical physics dealt with a "thermodynamic system", because "such as all material systems are": Thermodynamics was looked upon as a generalisation of ordinary mechanics. In the building up of his general theory, he followed the analogy with "theoretical mechanics", which took into account "simply mechanical systems ... which are capable of only one kind of action", namely "the performance of mechanical work". In this specific case, there was a function "which expresses the capability of the system for this kind of action", and the condition of equilibrium required that "the variation of this function shall vanish". In his more general mechanics, there were two functions corresponding to "the twofold capability of the system". According to Gibbs, every system "is capable of two different kinds of action upon external systems", and the two functions "afford an almost equally simple criterion of equilibrium".<sup>44</sup>

Immediately he put forward two complementary criteria of equilibrium for isolated systems, the first under the condition of a constant energy  $\varepsilon$ , and the second under the condition of a constant entropy  $\eta$ .

I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative. ... the condition of equilibrium may be written

$$(\delta\eta)_{\varepsilon} \leq 0$$

II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive. This condition may be written (1) (2)

$$(\delta\varepsilon)_{\eta} \geq 0 \quad 45$$

In other words, in transformations taking place at constant energy, the equilibrium corresponded to the maximum entropy, whereas in transformations taking place at constant entropy, the equilibrium corresponded to the minimum energy. As a first application, he considered "a mass of matter of various kinds enclosed in a rigid and fixed envelope", which

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<sup>42</sup> Massieu F. 1876, p. 43.

<sup>43</sup> He was an American engineer who had accomplished his scientific training in Paris, Berlin and Heidelberg: after having been appointed to the chair of mathematical physics at Yale in 1871, he published a series of fundamental papers under the common title "On the equilibrium of heterogeneous substances" in the *Transactions of the Connecticut Academy* in the years 1875-78.

<sup>44</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 55-6.

<sup>45</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 56.

was impermeable to both matter and heat fluxes. It was a very simplified case, wherein “Gravity, Electricity, Distorsion of the Solid Masses, or Capillary Tensions” were excluded.<sup>46</sup>

For every “homogeneous part of the given mass” Gibbs wrote down the equation

$$d\varepsilon = t d\eta - p dv,$$

which was nothing else but the first principle of thermodynamics. The first term in the second member was “the heat received”, and the second term “the work done”;  $v$ ,  $t$ , and  $p$  were volume, temperature, and pressure. Since Gibbs was not confining himself to “simply mechanical systems”, he let “the various substances  $S_1, S_2, \dots S_n$  of which the mass is composed” change their mass. As a consequence, the energy  $\varepsilon$  of the homogeneous component of the system could also depend on the corresponding variable masses  $m_1, m_2, \dots m_n$ :

$$d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots \mu_n dm_n,$$

where  $\mu_1, \mu_2, \dots \mu_n$  denoted “the differential coefficients of  $\varepsilon$  taken with respect to  $m_1, m_2, \dots m_n$ ”. In general, also “component substances which do not initially occur in the homogeneous mass considered” had to be taken into account. To the coefficients  $\mu_x$  Gibbs attributed the qualification of “potential for the substance  $S_x$ ”.<sup>47</sup>

In more complex systems, each homogeneous sub-set depended on the  $(n+2)$  variables  $t, v, m_1, m_2, \dots m_n$ , and the whole system depended on  $(n+2)v$ , wherein  $v$  was “the number of homogeneous parts into which the whole mass is divided”. The series of equations involving  $t, p$ , and  $\mu_1, \mu_2, \dots \mu_n$  contained exactly  $(v-1)(n+2)$  conditions among the  $(n+2)v$  variables. From the mathematical point of view, the remaining unknown variables were  $(n+2)$ . If the volume of “the whole mass”, and “the total quantities of the various substances” were known, then additional  $(n+1)$  conditions were available. Therefore only one unknown variable remained, but the knowledge of “the total energy of the given mass”, or alternatively “its total entropy”, led to “as many equations as there are independent variables”.<sup>48</sup> Alongside the algebraic problem, which Gibbs showed to be solvable, there was a very general physical problem: his general mathematical theory allowed him to derive the mechanical, thermal and chemical properties of a given physical system.

In the subsequent section, “Definition and Properties of Fundamental Equations”, Gibbs put forward other “fundamental equations” for a thermodynamic system, which involved new thermodynamic functions. The adjective “fundamental” meant that “all its thermal, mechanical, and chemical properties” of the system could be derived from them. He defined three functions

$$\psi = \varepsilon - t\eta \quad , \quad \chi = \varepsilon + pv \quad , \quad \zeta = \varepsilon - t\eta + pv.$$

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<sup>46</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 62.

<sup>47</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 63-5.

<sup>48</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 66.

Under specific conditions, the functions  $\psi$ ,  $\chi$ , and  $\xi$  assumed specific meanings, and led to new conditions of equilibrium.<sup>49</sup>

Gibbs was weaving the plot of a more general mechanics of equilibrium: he followed the track of Analytical Mechanics, but aimed at a wider-scope mechanics, which encompassed mechanics, thermodynamics and chemistry.

From the mathematical point of view, the fundamental functions  $\varepsilon$ ,  $\psi$ ,  $\chi$ , and  $\xi$  were interchangeable:  $\varepsilon$  as a function of volume and entropy could be replaced by  $\psi$  as a function of temperature and volume, by  $\chi$  as a function of entropy and pressure, or by  $\xi$  as a function of temperature and pressure. In brief, every fundamental function, associated to its two independent variables, defined a threefold system of co-ordinates, wherein the graph of the corresponding function  $z = f(x, y)$  could be drawn: four functions  $\varepsilon = f_\varepsilon(v, \eta)$ ,  $\psi = f_\psi(v, t)$ ,  $\chi = f_\chi(p, \eta)$ , and  $\xi = f_\xi(p, t)$  could be defined. We have in front of us a sort of symmetry, which transforms the space  $(v, \eta, \varepsilon)$  into the space  $(v, t, \psi)$ ,  $(p, \eta, \chi)$ , or  $(t, p, \xi)$ .<sup>50</sup>

He did not try to describe complex thermodynamic systems by means of mechanical models: on the contrary, purely mechanical systems were looked upon as specific instances of thermodynamic ones. The relationship between Mechanics and Thermodynamics consisted of a formal analogy: the mathematical structure of Mechanics offered a formal framework for the mathematical structure of Thermodynamics.

The same view was confirmed in a subsequent abstract Gibbs published in the *American Journal of Science* in 1878. From the outset he stressed the role of entropy, whose importance did “not appear to have been duly appreciated”: he claimed that “the general increase of entropy ... in an isolated material system” would “naturally” suggest that the maximum of entropy be identified with “a state of equilibrium”. He emphasised the role of the function  $\psi$  besides the functions  $\varepsilon$  and  $\eta$ , and the corresponding condition of equilibrium: when “the temperature of the system is uniform”, the condition of equilibrium could “be expressed by the formula”  $(\delta\psi)_t \geq 0$ . This inequality seemed to Gibbs suitable for equilibrium in “a purely mechanical system”, as a mechanical system was nothing else but “a thermodynamic system maintained at a constant temperature”. In the conceptual “transition” from “ordinary mechanics” to thermodynamics, the functions  $-\varepsilon$  and  $-\psi$  could “be regarded as a kind of force-function”, namely a generalisation of the concept of mechanical potential. The conditions of equilibrium  $(\delta\varepsilon)_\eta \geq 0$  and  $(\delta\psi)_t \geq 0$  would represent “extensions of the criterion employed in ordinary statics to the more general case of a thermodynamic system”.<sup>51</sup>

<sup>49</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, p. 89.

<sup>50</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 89, 93, and 116. See, in particular p. 93: “In the above definition we may evidently substitute for entropy, volume, and energy, respectively, either temperature, volume, and the function  $\psi$ ; or entropy, pressure, and the function  $\chi$ ; or temperature, pressure, and the function  $\xi$ .”

<sup>51</sup> Gibbs J.W. 1875-8, in Gibbs J.W. 1906, pp. 354-5. As remarked by Truesdell in the second half of the twentieth century, Gibbs built up a remarkable “axiomatic structure”, but his theory was “no longer the theory of motion and heat interacting, no longer thermodynamics, but only the beginnings of thermostatics” (Truesdell C. 1984, p. 20). The same concept is re-stated in Truesdell C. 1986, p. 104. Nevertheless Truesdell appreciated Gibbs’ stress on entropy. See Truesdell C. 1984, p. 26: “While he made his choice of entropy and absolute temperature as primitive concepts because that led to the most compact, mathematically efficient formulation of special problems as well as of the structure of his theory, of course he knew that entropy was not something obvious, not something that comes spontaneously to the burnt child who is learning to avoid the fire.”

The role of entropy, the structural analogy between Thermodynamics and Analytical Mechanics, and a unifying theoretical framework for physics and chemistry were also the main features of Helmholtz's pathway to Thermodynamics. At the beginning of the 1880s, he was a scientific authority: it is worth stressing that, in the scientific community of the time, he played a role quite different from Massieu, Rankine and Gibbs. After having made important contributions to physics and physiology, in 1882 Helmholtz put forward a mathematical theory of heat pivoted on the concept of "free energy".<sup>52</sup>

From the outset he put forward a unified theoretical approach for physical and chemical processes, based on the two principles of Thermodynamics. In particular, he found that thermo-chemical processes, in particular the production or dissolutions of chemical compounds, could not be interpreted in terms of mere production or consumption of heat. A more satisfactory theory had to take into account the fact that an amount of heat was not indefinitely convertible into an equivalent amount of work, according to Clausius' interpretation of the Carnot law.<sup>53</sup>

Helmholtz labelled  $\vartheta$  the absolute temperature, and  $p_\alpha$  the parameters defining the state of the body: they depended neither on each other nor on temperature. If Clausius had introduced "two functions of temperature and another parameter, which he called the Energy  $U$  and the Entropy  $S$ ", Helmholtz showed that "both of them can be expressed as differential quotients of a completely defined Ergal" or thermodynamic potential. If  $P_\alpha$  was the external force corresponding to the parameter  $p_\alpha$ , and  $P_\alpha \cdot dp_\alpha$  the corresponding work, then the total external work was  $dW = \sum_\alpha (P_\alpha \cdot dp_\alpha)$ . According to the first principle,

$$\mathfrak{J} \cdot dQ = dU + \sum_\alpha (P_\alpha \cdot dp_\alpha),$$

$$\mathfrak{J} \cdot dQ = \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \sum_\alpha \left( \frac{\partial U}{\partial p_\alpha} \cdot dp_\alpha \right) + \sum_\alpha (P_\alpha \cdot dp_\alpha).$$

Hierin bezeichnet  $\mathfrak{J}$  das mechanische Aequivalent der Wärmeeinheit und  $P_\alpha \cdot dp_\alpha$  die ganze bei der Aenderung  $dp_\alpha$  zu erzeugende, frei verwandelbare Arbeit, welche theils auf die Körper der Umgebung übertragen, theils in lebendige Kraft der Massen des Systems verwandelt werden kann.

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<sup>52</sup> After an academic career as a physiologist at Königsberg and Heidelberg universities, he had been appointed professor of physics at Berlin university in 1871, and then rector for the academic year 1877-8. He had delivered scientific lectures in many German universities and even in English universities and institutions, not to mention the honours received from French and English institutions. For a brief scientific biography, see Cahan D. 1993b, p. 3. For a general account of Helmholtz's contributions to Thermodynamics and Thermo-Chemistry, see Bierhalter G. 1993, and Kragh H. 1993.

<sup>53</sup> Helmholtz H. 1882, pp. 958-9. It is worth remarking that, since the 1860s, Thermo-Chemistry "rested on the Thomsen-Berthelot principle". According to that principle, chemical reactions "were accompanied by heat production", and in these processes "the most heat was produced". In the same years, Helmholtz himself and W. Thomson had put forward the "general idea that in a galvanic cell chemical energy was completely transformed into electric energy". Helmholtz realized that the second Principle of Thermodynamics required a reassessment of his previous point of view. See Kragh H. 1993, pp. 404 and 409.

Diese letztere ist eben auch als eine den inneren Veränderungen des Systems gegenüberstehende äussere Arbeit zu betrachten.<sup>54</sup>

Beside this generalisation of the first principle, Helmholtz put forward a similar generalisation of the second law. He defined the entropy  $S$  as  $dQ/\vartheta$ , or more specifically

$$dS = \frac{\partial S}{\partial \vartheta} \cdot d\vartheta + \sum_{\alpha} \left[ \frac{\partial S}{\partial p_{\alpha}} \cdot dp_{\alpha} \right].$$

Then he derived an equivalent expression from the first Principle:

$$\mathfrak{J} \cdot \frac{dQ}{\vartheta} = \frac{1}{\vartheta} \frac{\partial U}{\partial \vartheta} \cdot d\vartheta + \frac{1}{\vartheta} \sum_{\alpha} \left[ \left( \frac{\partial U}{\partial p_{\alpha}} + P_{\alpha} \right) \cdot dp_{\alpha} \right],$$

and the physical equivalence led to the mathematical relations

$$\mathfrak{J} \cdot \frac{\partial S}{\partial \vartheta} = \frac{1}{\vartheta} \cdot \frac{\partial U}{\partial \vartheta} \quad \text{and} \quad \mathfrak{J} \cdot \frac{\partial S}{\partial p_{\alpha}} = \frac{1}{\vartheta} \cdot \left( \frac{\partial U}{\partial p_{\alpha}} + P_{\alpha} \right). \quad ^{55}$$

From the second equation, a simple and interesting expression for generalised forces followed:

$$\mathfrak{J} \cdot \vartheta \cdot \frac{\partial S}{\partial p_{\alpha}} = \frac{\partial U}{\partial p_{\alpha}} + P_{\alpha} \quad \text{or} \quad P_{\alpha} = \frac{\partial}{\partial p_{\alpha}} \cdot (\mathfrak{J} \cdot \vartheta \cdot S - U).$$

The function  $\mathcal{F} = U - \mathfrak{J} \cdot \vartheta \cdot S$  played the role of a generalised potential for the forces  $P_{\alpha}$ :

$$P_{\alpha} = - \frac{\partial \mathcal{F}}{\partial p_{\alpha}}.$$

According to Helmholtz, the function  $\mathcal{F}$  represented the potential energy or the “Ergal” in the thermodynamic context. The functions  $U$  and  $S$  could be derived from  $\mathcal{F}$  by simple derivation:

$$\frac{\partial \mathcal{F}}{\partial \vartheta} = - \mathfrak{J} \cdot S, \quad \text{and} \quad U = \mathcal{F} + \mathfrak{J} \cdot \vartheta \cdot S \quad \text{or} \quad U = \mathcal{F} - \vartheta \cdot \frac{\partial \mathcal{F}}{\partial \vartheta}. \quad ^{56}$$

<sup>54</sup> Helmholtz 1882, pp. 966-7.

<sup>55</sup> Helmholtz H. 1882, p. 967.



The function  $\mathcal{F}$  also represented the “free energy”, namely the component of the internal energy which could be transformed into every kind of work. If  $U$  represented the total internal energy, the difference between  $U$  and  $\mathcal{F}$ , namely  $\mathfrak{J} \cdot \vartheta \cdot S$ , represented the “bound energy”, namely the energy stored in the system as a sort of *entropic* heat.<sup>57</sup>

In the second section of his paper, Helmholtz tried to re-interpret “the other two quantities  $dW$  and  $dQ$  which appears in Clausius’ equations”. For this purpose he found it necessary to introduce two differential operators: he labelled  $\delta$  the variation of whatever function  $\varphi$  when the parameters  $p_\alpha$  changed but the temperature did not, whereas the symbol  $d$  corresponded to a complete variation, when the temperature also changed. For a function  $\varphi$  of  $p_\alpha$  and  $\vartheta$ ,

$$\delta\varphi = \sum_{\alpha} \left( \frac{\partial\varphi}{\partial p_{\alpha}} dp_{\alpha} \right) \quad \text{and} \quad d\varphi = \delta\varphi + \frac{\partial\varphi}{\partial\vartheta} d\vartheta.$$

The external work or what he called “freely convertible external work”  $dW$  could be expressed in term of the new derivatives. Since  $P_{\alpha} = -\partial\mathcal{F}/\partial p_{\alpha}$ ,

$$dW = \sum (P_{\alpha} \cdot dp_{\alpha}) = \sum \left( -\frac{\partial\mathcal{F}}{\partial p} \cdot dp_{\alpha} \right) = -\delta\mathcal{F}^{58}$$

According to the new symbols, the first principle assumed the form

$$\mathfrak{J} \cdot dQ = dU - \delta\mathcal{F}.$$

The free energy represented only a part of the total energy  $U$ : the remaining part was labelled “bound energy” or “bound work” or  $\mathcal{G}$ . From the mathematical point of view,  $\mathcal{F} + \mathcal{G} = U$ . Helmholtz offered a mathematical and conceptual alternative to the first principle expressed in terms of  $W$  and  $Q$ :  $\mathcal{F} + \mathcal{G} = U$  instead of  $\mathfrak{J} \cdot dQ = dU + dW$ .

Helmholtz’s *mechanical* approach to Thermodynamics was in accordance with the tradition of Analytical Mechanics. In the subsequent years, he tried to follow a slightly different pathway, wherein some hypotheses on the mechanical *nature* of heat were put forward. He tried to give a microscopic explanation of heat, without any recourse to specific mechanical models. This point deserves to be mentioned: in 1884, in the paper “Principien der Statik monocyklischer Systeme”, Helmholtz followed an intermediate pathway, which was neither Boltzmann nor Massieu-Gibbs’ pathway. He introduced a microscopic Lagrangian coordinate, corresponding to a fast, hidden motion, and a set of macroscopic coordinates,

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<sup>56</sup> Helmholtz H. 1882, pp. 968-9. As I have shown in the previous chapter, the last two equations had already been derived from the French engineer Massieu: Helmholtz did not seem aware of Massieu’s result, which had probably not crossed the France borderlines.

<sup>57</sup> Helmholtz H. 1882, p. 971.

<sup>58</sup> Helmholtz H. 1882, pp. 972-3.

corresponding to slow, visible motions. The energy associated with the first coordinate corresponded to thermal energy, whereas the energy associated with the others corresponded to external thermodynamic work.<sup>59</sup>

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<sup>59</sup> Buchwald stressed that Helmholtz put forward an Analytical-Mechanical approach to the microscopic level “without simultaneously adopting a fully reductionist atomistics” (Buchwald J.Z. 1993, pp. 335). See also Cahan D. 1993b, p. 10. For a detailed analysis of Helmholtz’s 1884 paper, and similar theoretical researches which appear in the sixth volume of his *Vorlesungen über Theoretische Physik*, see Bierhalter G. 1993, pp. 437-42.

#### 4. Physical and mathematical symmetries

In the meantime, in 1880, the young German physicist Max Planck was pursuing a slightly different target. He lamented that the theory of mechanical processes, in particular mechanical elasticity, had been put forward without any connection with the thermal properties of bodies, and the thermal actions on them. He aimed at filling the gap between thermodynamics and the theory of elasticity. In the dissertation *Gleichgewichtszustände isotroper Körper in verschiedenen Temperaturen*, which he published in order to be given the *venia legendi*, he outlined a mathematical theory where the mechanics of continuous media merged with thermal processes. He relied on the two principles of “the mechanical theory of heat”, and “specific assumptions on the molecular structure (Beschaffenheit) of bodies” were “not necessary”. In accordance with this theoretical option, he assumed that isotropic bodies consisted of “continuous matter”.<sup>60</sup>

The body could be subject to “an external pressure”, and the condition of equilibrium was assured by the counteraction of “internal elastic forces”. Both mechanical work and fluxes of heat could act on the body: under those actions, both the reciprocal of density (“spezifische Volumen”) and temperature could change from  $(v; T)$  to  $(v'; T')$ . In particular the geometrical co-ordinates of a point inside the body underwent a transformation in accordance with the equations

$$x = x_0 + \xi; \quad y = y_0 + \eta; \quad z = z_0 + \zeta,$$

where  $x_0, y_0, z_0$  are the initial values and  $\xi, \eta, \zeta$  the infinitesimal variation. The elastic forces acting on the surfaces parallel to the planes YZ, ZX, and XY were labelled by Planck  $X = (X_x, X_y, X_z)$ ,  $Y = (Y_x, Y_y, Y_z)$ , and  $Z = (Z_x, Z_y, Z_z)$ , where  $X_y = Y_x, Y_z = Z_y, Z_x = X_z$ , “as usually assumed in the theory of elasticity”.<sup>61</sup>

In the internal part of the body, the conditions of equilibrium were

$$\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} = 0,$$

$$\frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} = 0,$$

$$\frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} = 0,$$

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<sup>60</sup> Planck became *Privatdocent* at the University of Munich in 1880, and was appointed as extraordinary professor of physics at the University of Kiel in 1885. In 1889, two years after Kirchhoff's death, he became assistant professor at the University of Berlin, and director of the Institute for Theoretical Physics: in 1892 he was appointed ordinary professor. See McCormach R. and Jungnickel C. 1986, vol. 2, pp. 51-2, 152, and 254, and Gillispie C.C. (ed.), Volume XI, p. 8.

<sup>61</sup> Planck M. 1880, pp. 3-4. On the developments of the theory of elasticity in the first half of the XIX century, see Darrigol O. 2002, in particular sections from 2 to 6.

whereas on the external surface they were

$$\begin{aligned}\Xi + \alpha X_x + \beta X_y + \gamma X_z &= 0 \\ \text{H} + \alpha Y_x + \beta Y_y + \gamma Y_z &= 0, \\ \text{Z} + \alpha Z_x + \beta Z_y + \gamma Z_z &= 0\end{aligned}$$

where  $(\Xi, \text{H}, \text{Z})$  were the components of the external force,  $(\alpha, \beta, \gamma)$  the directive cosines, and  $d\Phi = \Xi \cdot d\xi + \text{H} \cdot d\eta + \text{Z} \cdot d\zeta$  the work done by the external force.<sup>62</sup>

The first principle of thermodynamics allowed a unified account of phenomena, and a unified overview on physical space. If  $T' = T + \tau$  was the relationship between initial and final temperature in the course of a transformation, Planck specified that, in the end, energy depended on  $\tau$  and on the derivative of  $(\xi, \eta, \zeta)$  with reference to  $(x, y, z)$ . In particular it depended on the seven new variables  $\delta\tau$  and  $\delta x_x, \delta y_y, \delta z_z, \delta x_y + \delta y_x, \delta y_z + \delta z_y, \delta z_x + \delta x_z$ , where

$$\begin{aligned}x_x &= \frac{\partial \xi}{\partial x}, y_y = \frac{\partial \eta}{\partial y}, z_z = \frac{\partial \zeta}{\partial z}, \\ x_y &= \frac{\partial \xi}{\partial y}, y_x = \frac{\partial \eta}{\partial x}, y_z = \frac{\partial \eta}{\partial z}, z_y = \frac{\partial \zeta}{\partial y}, z_x = \frac{\partial \zeta}{\partial x}, x_z = \frac{\partial \xi}{\partial z}.\end{aligned}\quad ^{63}$$

After having simplified typographically “the dilatation of the unitary volume” by means of a new variable  $\Theta = (x_x + y_y + z_z)$ , Planck chose an expression for the energy  $dU$  of “the element of mass  $dM$ ” in terms of the new variables:

$$\begin{aligned}dU &= dM[\text{const} + k \cdot \tau + l \cdot \Theta + \frac{m}{2} \cdot \tau^2 + p \cdot \tau \Theta + \frac{q}{2} \cdot \Theta^2 \\ &\quad + r \cdot (x_x^2 + y_y^2 + z_z^2) + \frac{r'}{2} (x_y^2 + y_z^2 + z_x^2)].\end{aligned}$$

The formal structure of entropy was not so different from that of energy:

$$\begin{aligned}dS &= dM[\text{const} + k' \cdot \tau + l' \cdot \Theta + \frac{m'}{2} \cdot \tau^2 + p' \cdot \tau \Theta + \frac{q'}{2} \cdot \Theta^2 \\ &\quad + r' \cdot (x_x^2 + y_y^2 + z_z^2) + \frac{r'}{2} (x_y^2 + y_z^2 + z_x^2)],\end{aligned}$$

Planck could compare the two expression and the two sets of coefficients by means of the relationship between energy and entropy:

<sup>62</sup> Planck M. 1880, pp. 4-6. He specified that elastic forces could not rely on “a potential”, because “they depended on temperature” (p. 8).

<sup>63</sup> Planck M. 1880, pp. 9-10.

$$dS = \frac{dQ}{T} = \frac{dU - d\Phi}{T}.^{64}$$

The comparison gave rise to seven relationships between the derivatives of  $u$  and  $s$ , namely the densities of energy and entropy:

$$\frac{\partial u}{\partial \tau} = T' \frac{\partial s}{\partial \tau},$$

$$\frac{\partial u}{\partial x_x} + v' X_x = T' \frac{\partial s}{\partial x_x},$$

$$\frac{\partial u}{\partial y_y} + v' Y_y = T' \frac{\partial s}{\partial y_y},$$

$$\frac{\partial u}{\partial z_z} + v' Z_z = T' \frac{\partial s}{\partial z_z},$$

$$\frac{\partial u}{\partial x_y} + v' X_y = T' \frac{\partial s}{\partial x_y},$$

$$\frac{\partial u}{\partial y_z} + v' Y_z = T' \frac{\partial s}{\partial y_z},$$

$$\frac{\partial u}{\partial z_x} + v' Z_x = T' \frac{\partial s}{\partial z_x}.$$

The first relationship led to

$$k = Tk', \quad m = Tm' + k', \quad p = Tp'.$$

The second, third and fourth led to

$$X_x = \frac{Tl' - 1}{v} + \frac{l'}{v} \cdot \tau - \frac{(q - l) - T(q' - l')}{v} \cdot \Theta - \frac{2(r - Tr')}{v} \cdot x_x, \quad (1)$$

and similar expressions for  $Y_y$  and  $Z_z$ .

The fifth, sixth and seventh led to

$$X_y = -\frac{r - Tr'}{v} \cdot x_y, \quad (2)$$

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<sup>64</sup> Planck M. 1880, pp. 12-6.

and other similar expressions for  $Y_z$  and  $Z_x$ .<sup>65</sup>

The combinations of coefficients in (1) and (2) could be typographically simplified in accordance with simple physical remarks and the typographical tradition of the theory of elasticity. If the first expression in (1) corresponded to the external pressure, the third expression corresponded to the traditional term  $\lambda$ , whereas the fourth expression in (1) and that in (2) corresponded to the traditional term  $\mu$ . In brief:

$$P = \frac{Tl' - 1}{v},$$

$$\lambda = \frac{(q - l) - T(q' - l')}{v},$$

$$\mu = \frac{r - Tr'}{v},$$

and therefore

$$X_x = P + \frac{l'}{v} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x,$$

$$X_y = -\mu \cdot x_y.$$
<sup>66</sup>

Internal energy, entropy, and the specific heats could be expressed in terms of  $k, \lambda, \mu$ , and the other coefficient  $\alpha$ , which represented “the variation of the specific volume with temperature, at constant pressure”, namely

$$\alpha = \left( \frac{v' - v}{T' - T} \right)_P = v \left( \frac{\Theta}{\tau} \right)_P.$$

If  $u = k \cdot \tau + \left[ \alpha \left( \lambda + \frac{2}{3} \mu \right) T - Pv \right] \cdot \Theta$  and  $s = \frac{k}{T} \cdot \tau + \alpha \left( \lambda + \frac{2}{3} \mu \right) \cdot \Theta$ , then the constant  $k$  could be identified with “the specific heat at constant volume”. Planck showed that the specific heat at constant pressure could be expressed by

$$c = k + \alpha^2 \left( \lambda + \frac{2}{3} \mu \right) \frac{T}{v}.$$

In the end,

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<sup>65</sup> Planck M. 1880, pp. 17-8.

<sup>66</sup> Planck M. 1880, p. 19. For the introduction of parameters  $\lambda$  and  $\mu$  in the theory of elasticity in the first half of the XIX century, see Darrigol O. 2002, pp. 110, 113, and 122-4.

$$X_x = P + \frac{\alpha(3\lambda + 2\mu)}{3\nu} \cdot \tau - \lambda \cdot \Theta - 2\mu \cdot x_x. \text{ } ^{67}$$

In brief, energy, entropy, and elastic stresses depended on a combination of mechanical and thermal variables, which were multiplied by a combination of mechanical and thermal coefficients. In the remaining part of the chapter, Planck showed some applications to specific states of matter: solid bodies, fluid drops, and vapours and gases.

Two years later, in the paper “Vaporising, melting, and sublimating” (“Verdampfen, Schmelzen und Sublimieren”), he claimed once again that his theoretical approach was based on “the two principles of the mechanical theory of heat”, and was “completely independent of any assumption on the internal structure of bodies”. In physical-chemical transformations there were “several states corresponding to relative maxima of entropy”, but there was only one “stable state of equilibrium”, which corresponded to “the absolute maximum of entropy”: the others states were nothing more than “unstable states of equilibrium”. In the last part of his paper, Planck stressed that his previous statements were pure consequences of a more general law: “in natural processes, the sum of the entropies of the parts of a given body does increase”. Only in reversible processes, the entropy would remain unchanged, but those kinds of processes did “not really exist”: they could “be looked upon as merely ideal”. When a physical system reached the maximum entropy, “no transformation” could “take place any more”. The maximum entropy would therefore correspond to “a stable state of equilibrium”, and this correspondence between entropy and equilibrium would represent “the best way to base the search for the conditions of equilibrium on rational grounds”, both in physics and chemistry.<sup>68</sup>

In 1885 the German speaking physicist Arthur von Oettingen, who held the chair of Physics in Dorpat University (now Tartu, Estonia), undertook an even more ambitious design: a formal theory, where mechanical work and fluxes of heat represented the starting point of a dual mathematical structure. A large family of thermal and mechanical “capacities” emerged.<sup>69</sup>

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<sup>67</sup> Planck M. 1880, pp. 21-3.

<sup>68</sup> Planck M. 1882, pp. 452 and 472. The distinctive feature of an unstable equilibrium was the establishment of “a finite change of state” as a consequence of “an arbitrary small change in external conditions”. According to Planck, a specific instance of unstable equilibrium was offered by “explosions in mixtures of gases”, where the addition of “a convenient but arbitrary small amount of energy” could trigger off sudden and dramatic transformations (*Ibidem*, p. 474). Planck held the same position on the foundation of Thermodynamics for many years. In 1891, in a paper he read at the annual meeting of German scientists, Planck claimed that Maxwell and Boltzmann’s skilful “analysis of molecular motion” was not “adequately rewarded by the fruitfulness of the results gained”. In particular, he found that the kinetic theory was not at ease with phenomena placed on the borderline between Physics and Chemistry: he did not expect that it could “contribute to further progress” in that field. See Kuhn T.S. 1987, p. 22. Similar remarks can be found in the book on the foundation of Thermochemistry Planck published in 1893.

<sup>69</sup> After having studied at Dorpat, in Livonia (now Tartu, Estonia), he spent some years in Augustine Césaire Bequerel and Henri Victor Régnault’s laboratories in Paris, and then in Heinrich Gustav Magnus, Johann Christian Poggendorff and Heinrich Wilhelm Dove’s laboratories in Berlin. In 1868 he became Professor of Physics at Dorpat.

His very long paper was published in the *Mémoires de l'Académie impériale des sciences de Saint-Pétersbourg*, and its complete title was “Die thermodynamischen Beziehungen antithetisch entwickelt” (Antithetically developed thermodynamic connections). The German adjective and adverb “antithetisch” might be interpreted in two different ways: either the opposition to traditional approaches to thermodynamics, or the development of antithetical or complementary mathematical relations in the body of knowledge of thermodynamics. In some way, both interpretations are suitable, because both of them manage to catch the original content of the paper. From the outset the author stressed that the great number of “multifarious relations” in physics could be encompassed by “a unitary viewpoint”, and could be “grouped and ordered in a rigorous system”. Thermodynamics in particular was in that favourable condition, even though, generally speaking, “textbooks failed to fulfil that unitary commitment”. Oettingen specified that “the new exposition of the subject matter” was developed in accordance with a dual approach: for every set of relations, a set of complementary ones emerged. From the typographical point of view, this complementarity led to a two-columns exposition, where two sets of variables, functions, and laws were compared to each other, and sometimes the mathematical symmetries were explicitly stressed.<sup>70</sup>

The whole body of knowledge of thermodynamics could be based on four “main variables” or parameters, and two kinds of energy. In the left column he put temperature and entropy, and the corresponding energy, which was “the current energy  $Q$ ”, or in other words the flux of heat. In the right column he put volume and pressure, and the corresponding energy, which was the “potential energy  $S$ ”, namely the mechanical energy which actually appeared under the form of mechanical work. In brief

$$dQ = t \cdot du,$$

$$dS = -p \cdot dv,$$

where  $t$  was “the absolute temperature” and  $u$  “the entropy or Adiabate”. Temperature was a measure of the amount of “current energy of molecules”.

where  $p$  was “the pressure” and  $v$  “the specific volume”. Pressure was the measure of “the dead energy of the body against the outer wall”

If a flux of “current energy” led necessarily to a variation of entropy in the physical system, a flux of “potential energy” led necessarily to a variation in the volume of the system. In brief

$$du = \frac{dQ}{t},$$

$$dv = \frac{dS}{p}.$$

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<sup>70</sup> Oettingen A. 1885, p. 1. His long essay was divided into three parts: “General relations of Thermodynamics for every state of aggregation” (“Allgemeine Beziehungen der Thermodynamik, für alle Aggregatformen”), “Theory of thermal heat capacity based on a new hypothesis” (“Theorie der thermischen Wärmecapazität auf Grund einer neuen Hypothese”), and “Theory of gases” (“Theorie der Gase”).



Conversely, a system at “constant Adiabate” could undergo transformations only by a transfer of “potential energy”, and a system at “constant volume” only by a transfer of “current energy”.<sup>71</sup>

In general the state of a system could be described by two parameters among the four  $t, u, p, v$ , but the two more meaningful representations corresponded to the choices  $(u, t)$  and  $(v, p)$ . After having discussed about the opportunity to label “Adiabate” or “Entropie” the differential form  $dQ/T$ , Oettingen insisted on the physical and linguistic symmetry between thermal and mechanical variables and functions. Within the framework of his combinatorial mathematical physics, many “differential quotients” or “coefficients” found room: among them, some enjoyed a relevant physical meaning and deserved a specific label. For instance,

Coefficients of compression:	$\left(\frac{dp}{dv}\right)_{u/t}$	$\left(\frac{dt}{du}\right)_{p/v}$
Coefficients of expansion:	$\left(\frac{dv}{dt}\right)_{p/u}$	$\left(\frac{du}{dp}\right)_{t/v}$
Coefficients of tension:	$\left(\frac{dp}{dt}\right)_{v/u}$	$\left(\frac{dt}{dp}\right)_{v/u}$

The subscript pointed out the constancy of the corresponding variable. Even more meaningful it appeared the list of “energy coefficients” or “capacities”: among them, the ordinary heat capacities could be found. That list was a dual one indeed: if on the left the list of “heat capacities” (“Wärmecapacitäten”) was displayed, on the right we can see the list of “work capacities” (“Arbeitscapacitäten”). The whole list required series of two adjectives for the substantive “capacity”.

Thermal heat capacities:

$$\left(\frac{dQ}{dt}\right)_v = C_v$$

$$\left(\frac{dQ}{dt}\right)_p = C_p$$

Thermal work capacities:

$$\left(\frac{dS}{dt}\right)_u = \Phi_u$$

$$\left(\frac{dS}{dt}\right)_p = \Phi_p$$

Barometric heat capacities:

$$\left(\frac{dQ}{dp}\right)_v = F_v$$

$$\left(\frac{dQ}{dp}\right)_t = F_t$$

Barometric work capacities:

$$\left(\frac{dS}{dp}\right)_u = \Gamma_u$$

$$\left(\frac{dS}{dp}\right)_t = \Gamma_t$$

Metric heat capacities:

Entropic work capacities:

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<sup>71</sup> Oettingen A. 1885, pp. 2-3.

$$\begin{aligned} \left(\frac{dQ}{dv}\right)_t &= L_t & \left(\frac{dS}{du}\right)_t &= \Lambda_t \\ \left(\frac{dQ}{dv}\right)_p &= L_p & \left(\frac{dS}{du}\right)_p &= \Lambda_p. \end{aligned} \quad ^{72}$$

At the same time, other algebraic relations and symmetries emerged.

$$\begin{aligned} F_v &= C_v \left(\frac{dt}{dp}\right)_v & \Phi_u &= \Gamma_u \left(\frac{dp}{dt}\right)_u \\ L_t &= F_t \left(\frac{dp}{dv}\right)_t & \Lambda_p &= \Phi_p \left(\frac{dt}{du}\right)_p \\ C_p &= L_p \left(\frac{dv}{dt}\right)_p & \Gamma_t &= \Lambda_t \left(\frac{du}{dp}\right)_t \\ F_v \cdot L_t \cdot C_p + C_v \cdot F_t \cdot L_p &= 0 & \Phi_u \cdot \Gamma_t \cdot \Lambda_p + \Phi_p \cdot \Gamma_u \cdot \Lambda_t &= 0. \end{aligned} \quad ^{73}$$

The above relations could find a meaningful simplification in the case of gases, or precisely the so-called ideal gases. In this case, three conditions had to be fulfilled:

1. the specific heats  $C_v$  and  $C_p$  had to be constant,
2. the internal energy  $E$  depended only on temperature, and
3. the equation of state for ideal gas  $p \cdot v = Rt$  was assumed.

In this case, a series of simple relations followed:

$$C_v = \Phi_u = \text{const.}, \quad C_p = \Phi_u - \Phi_p = \text{const.}, \quad L_t = p, \quad \Gamma_t = v, \quad \Lambda_t = -t. \quad ^{74}$$

Oettingen was aware of the existence of recent abstract approaches to Thermodynamics. In particular, he attempted to link his approach to Helmholtz's recent developments, and in this context the concepts of "free and bound energy" played a relevant role. In reality, in accordance with his dual and complementary framework, he relied on a series of four functions, "free, bound, total and lost energies" ("freie, gebundene, totale und verlorene Energie"). A two-fold representation, and an intrinsic symmetry emerged once again. He first introduced the two functions "bound energy  $G = t \cdot u$ " and "lost energy  $V = -p \cdot v$ ", and then defined "free energy" and "total energy" as

<sup>72</sup> Oettingen A. 1885, pp. 4-8. A graphic interpretation of heat and work capacities was available both in  $(u, t)$  and  $(v, p)$  spaces. In particular, the values of  $C_v$  and  $C_p$  could be found in the horizontal axes  $u$  of the plane  $(u, t)$ , and the values of  $\Gamma_u$  and  $\Gamma_t$  could be found on the horizontal axes  $v$  of the plane  $(v, p)$ .

<sup>73</sup> Oettingen A. 1885, pp. 9-10.

<sup>74</sup> Oettingen A. 1885, pp. 16-7.

$$\mathcal{F} = E - \mathcal{G} = E - t \cdot u$$

$$\mathcal{T} = E - \mathcal{V} = E - (-p \cdot v)$$

The differentiation of the functions yielded:

$$dE = d\mathcal{F} + d\mathcal{G} = dQ + dS$$

$$dE = d\mathcal{T} + d\mathcal{V} = dQ + dS$$

$$d\mathcal{G} = t \cdot du + u \cdot dt = dQ + u \cdot dt$$

$$d\mathcal{V} = -p \cdot dv - v \cdot dp = dS - v \cdot dp$$

$$d\mathcal{F} = dQ + dS - t \cdot du - u \cdot dt = dS - u \cdot dt$$

$$d\mathcal{T} = dQ + dS + p \cdot dv + v \cdot dp = dQ - (-v \cdot dp).^{75}$$

The two couples of functions or potentials  $(\mathcal{F}; \mathcal{G})$  and  $(\mathcal{T}; \mathcal{V})$  allowed physicists to split internal energy into two parts, and the split could be performed in two different ways. Moreover, if the traditional split  $dE = dQ + dS$  of the *state function*  $E$  did not lead to *state functions* or potentials, the two new splits led to two couples of *state functions*. In Oettingen's dual framework, free energy and total energy appeared as the generalisation of mechanical work and flux of heat, or better a sort of actual work and heat, once some kind of *disturbing terms* were subtracted. In isothermal and iso-entropic processes, the mechanical feature of "free energy" emerged, and conversely the thermal feature of "total energy" emerged in isobaric and iso-volumic processes. When his discussion is translated into an ordered list of mathematical expressions, the symmetries between the couples  $(\mathcal{F}; \mathcal{G})$  and  $(\mathcal{T}; \mathcal{V})$  is really astonishing.

Iso-thermal processes:  $dt = 0$

Iso-baric processes:  $dp = 0$

$$d\mathcal{F} = dS$$

$$d\mathcal{T} = dQ$$

$$d\mathcal{G} = dQ$$

$$d\mathcal{V} = dS$$

Iso-entropic processes:  $du = 0$  and  $dQ = 0$

Iso-volumic processes:  $dv = 0$  and  $dS = 0$

$$d\mathcal{G} = u \cdot dt$$

$$d\mathcal{V} = -v \cdot dp$$

$$d\mathcal{F} = dS - u \cdot dt = dS - d\mathcal{G}$$

$$d\mathcal{T} = dQ - (-v \cdot dp) = dQ - d\mathcal{V}$$

$$\rightarrow dS = d\mathcal{F} + d\mathcal{G}$$

$$\rightarrow dQ = d\mathcal{T} + d\mathcal{V}.^{76}$$

He criticised the concepts of "disordered motion" and "measure of disorder" when referred to entropy, because the "complexity of the concept of Adiabate" required that it was

<sup>75</sup> Oettingen A. 1885, pp. 21-2.

<sup>76</sup> Oettingen A. 1885, pp. 21-3. With regard to the thermodynamic potentials, he also acknowledged the contributions of Massieu, Maxwell, and Gibbs.

associated with “a plurality of conditions”. Moreover, from the point of view of physical dimensions, entropy or Adiabate was quite different from the living force of molecules, however disordered it may be. It appeared to Oettingen that perhaps the concept of “bound energy could be put in connection with a disordered motion”, but every “overlap between that disorder and the function  $u$  had to be excluded”. Entropy was a physical entity not so different from volume, and as such it could never become negative. In a body, “the content of heat could not be completely stolen”, in the same way that its volume could also not be. In other words, the content of disordered motion could not vanish: in no way could “absolute immobility” be actually realized.<sup>77</sup>

In the last pages of the first part of his essay, Oettingen showed that even Gibbs’ third potential  $\mathcal{N} = E - tu + pv$  could find room in his mathematical framework: it could be expressed alternatively as

$$\mathcal{N} = \mathcal{F} + \mathcal{T} - E \quad \text{or} \quad \mathcal{N} = E - \mathcal{G} - \mathcal{V}.$$

As a further combinatorial synthesis he displayed the derivatives of the five functions  $\mathcal{F}, \mathcal{G}, \mathcal{T}, \mathcal{V}, \mathcal{N}$  with reference to the four basic parameters  $p, v, t, u$ . Every derivative could be performed under the condition of constancy of one of the other parameters. In other words, those derivatives had the formal structure

$$\left( \frac{dP_k}{dx_j} \right)_{x_l} \quad k=1,2,3,4,5; \quad j,l=1,2,3,4,$$

where  $P_k$  represents the five potentials, and  $x_k, x_l$  two among the four basic parameters. As a whole, 60 derivatives could be written down ( $5 \times 4 \times 3$ ), and each of them corresponded to a specific combination of parameters and “capacities”. The list could be reversed, and every basic parameter and every “capacity” corresponded to some derivatives of thermodynamic potentials. In brief:

$$u = - \left( \frac{d\mathcal{F}}{dt} \right)_v = \left( \frac{d\mathcal{G}}{dt} \right)_u = - \left( \frac{d\mathcal{N}}{dt} \right)_p; \quad t = \left( \frac{d\mathcal{T}}{du} \right)_p = \left( \frac{d\mathcal{G}}{du} \right)_t;$$

$$v = \left( \frac{d\mathcal{T}}{dp} \right)_u = - \left( \frac{d\mathcal{V}}{dp} \right)_v = \left( \frac{d\mathcal{N}}{dp} \right)_t; \quad p = \left( \frac{d\mathcal{F}}{dv} \right)_t = \left( \frac{d\mathcal{V}}{dv} \right)_p.$$

A well-defined symmetry shows that the second line can be obtained from the first by means of the exchanges of potentials  $\mathcal{F} \leftrightarrow \mathcal{T}$  and  $\mathcal{G} \leftrightarrow \mathcal{V}$ , and the exchanges of variables  $t \leftrightarrow p$  and  $u \leftrightarrow v$ .

With regard to capacities, both thermal and mechanical, internal energy had to be added to the list of potentials to be derived. In brief:

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<sup>77</sup> Oettingen A. 1885, pp. 24-5.

$$\begin{aligned}
C_v &= \left( \frac{dE}{dt} \right)_v, & C_p &= \left( \frac{dT}{dt} \right)_p; & \Gamma_u &= \left( \frac{dE}{dp} \right)_u, & \Gamma_t &= \left( \frac{dF}{dp} \right)_v \\
F_v &= \left( \frac{dE}{dp} \right)_v, & F_t &= \left( \frac{dG}{dp} \right)_t; & \Phi_u &= \left( \frac{dE}{dt} \right)_u, & \Phi_p &= \left( \frac{dV}{dt} \right)_p \\
L_t &= \left( \frac{dG}{dv} \right)_t, & L_p &= \left( \frac{dT}{dv} \right)_p; & \Lambda_p &= \left( \frac{dV}{du} \right)_p, & \Lambda_t &= \left( \frac{dF}{du} \right)_t.
\end{aligned}$$

Once again, we see that the above mentioned symmetries operate between the two couples of every line.<sup>78</sup>

In the end Oettingen pointed out the generality of his approach, which was valid “for any state of aggregation”, even though the theory required “reversible processes”. The choice of basic parameters or variables did not affect such a generality: in particular, the variable  $v$  could be replaced by a set of geometrical parameters, “just as Helmholtz had done”. Nevertheless he did not specify how the wonderful symmetries of the equations might be preserved in the case of irreversible processes. He thought he had fulfilled his explicit “intention”, namely to collect “into a self-contained system all existing knowledge” on thermodynamics.<sup>79</sup>

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<sup>78</sup> Oettingen A. 1885, pp. 23 and 26-9. He was extremely accurate in displaying long series of derivatives, but did not stress the symmetries emerging from the combinatorial game.

<sup>79</sup> Oettingen A. 1885, p. 31.

### 5. The general equations of Thermodynamics

The following year the young mathematical physicist Pierre Duhem published a book on thermodynamic potentials and their applications to electrical and chemical processes. He recollected the main steps of Gibbs' logical pathway: he listed Gibbs' potentials  $\psi = E(U - TS)$  and  $\zeta = E(U - TS) + pv$ , which were quite similar to Massieu's functions, and Gibbs' laws of equilibrium involving energy and entropy. He also mentioned Helmholtz's "distinction between two kinds of energy, the free energy ... and the bound energy": Helmholtz's free energy  $F$  was nothing else but Gibbs' function  $\psi$ , which in its turn was proportional to Messieu's "fonction caractéristique"  $H$ :  $F = E(U - TS) = \psi = -EH$ .<sup>80</sup>

Duhem wrote the first principle of Thermodynamics as

$$dQ + Ad \sum \frac{mv^2}{2} = -dU + A d\tau_e,$$

where  $dQ$  was a quantity of heat,  $Ad \sum \frac{mv^2}{2}$  the variation of living force,  $d\tau_e$  the variation of the external work,  $A$  the thermal equivalent of the mechanical work, and  $dU$  represented "the total differential of a function well specified apart from a constant". With regard to the second principle, Duhem reminded the reader of Clausius' interpretation of  $dQ/T$  as "unit of transformation or merely transformation", and the corresponding theorem, "[t]he sum of transformations throughout a close everisible cycle is nought". Then he reminded the reader of the extension of Clausius' theorem to reversible "transformations different from a closed cycle": the integral  $\int dQ/T$  depended "only on the initial and final state of the system". Subsequently Clausius had included non-reversible closed cycles, which had led to a more general statement "[t]he algebraic sum of transformations occurring in a non-reversible closed cycle must be positive". Including "whatever series of non-reversible transformations", he had further widened the scope of the principle: the key concept was the "non-compensated transformation". If a physical system passed from the initial state (0) to the final state (1) through different steps, one of them being at least non-reversible, and then came back to (0) through a series of reversible (r) steps,

$$\int \frac{dQ}{T} > 0 \quad \text{namely} \quad \int_0^1 \frac{dQ}{T} + \int_{(r) 1}^0 \frac{dQ}{T} > 0.$$

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<sup>80</sup> Duhem P. 1886, pp. VI and IX. Physical remarks and historical reconstructions are tightly linked to each others: it is one of the long-lasting hallmarks of Duhem's scientific practice. The coefficient  $E$  was nothing else but "l'équivalent mécanique de la chaleur". The relationship between the mechanical equivalent of heat  $E$  and the thermal equivalent of mechanical work  $A$  is of course  $EA = 1$ .

Making use of the definition of entropy  $\int_{(r)1}^0 \frac{dQ}{T} = S_1 - S_2$ , Duhem reported Clausius' result as

$$\int_0^1 \frac{dQ}{T} + S_1 - S_2 = N > 0.$$

On the track of Clausius' theoretical pathway, Duhem qualified  $N$  as “*the sum of non-compensated transformations*”. In the specific case of isothermal transformations, he could write (5)  $N = A(\tau/T)$ , where  $\tau$  could be interpreted as “an amount of work which can be naturally qualified as *non-compensated work*”.<sup>81</sup>

These concepts emphasised the formal analogy between Mechanics and Thermodynamics. For systems without any macroscopic living force, the first Principle became  $dQ = -dU + A d\tau_e$ , and for isothermal transformations, the other equations became

$$\tau = ETN \quad \text{and} \quad N = S_1 - S_0 + \frac{1}{T} \int_0^1 dQ.$$

A new mathematical expression for the non-compensated work  $\tau$  followed:

$$\tau = ET(S_1 - S_0) - E(U_1 - U_0) + \int_0^1 d\tau_e.$$

If external forces stemmed “from a potential  $W$ ”, the last equation became

$$\tau = ET(S_1 - S_0) - E(U_1 - U_0) + W_0 - W_1,$$

and Duhem could define a more general potential  $\Omega = E(U - TS) + W$ . The very synthetic expression  $\tau = \Omega_0 - \Omega_1$  (8) followed: in his words, “non-compensated work ... is equal to the opposite of the variation of  $\Omega$ ” in an isothermal transformation. The analogy between mechanics and thermodynamics led Duhem to choose the name “*thermodynamic potential of the system*” for the function  $\Omega$ .<sup>82</sup>

In two specific instances, at constant volume or pressure, Duhem's thermodynamic potential had important consequences from the theoretical point of view, and from the point

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<sup>81</sup> Duhem P. 1886, pp. 3-7. It is worth noticing that Duhem labelled “principle” rather “theorem” Clausius' statement about entropy or “transformation”, which corresponded to the second principle of thermodynamics. It is also worth noticing that the word “transformation” assumed two different meanings in Duhem's paper: the general meaning of “change”, and the specific meaning of “entropy”.

<sup>82</sup> Duhem P. 1886, pp. 7-8.

of view of “applications”. In the first case,  $W = 0$ , and the potential  $\Omega$  became  $F = E(U - TS)$ , which was “Helmholtz’s free energy” or Gibbs’  $\psi$  function. In the second case,  $dW = pdv = d(pv)$ , and the potential  $\Omega$  became  $\Phi = E(U - TS) + pv$ , which was “nothing else but Gibbs’  $\zeta$  function”.<sup>83</sup>

After three years, while he was lecturing at Lille university, Duhem began to outline a systematic design of rephrasing Thermodynamics. He published a paper in the official revue of the *Ecole Normale Supérieure*, wherein he displayed what he called the “general equations of Thermodynamics”. Once again he made reference to the recent history of Thermodynamics. Apart from Clausius, who “had already devoted a paper to a systematic review on the equations of Thermodynamic”, four scientists were credited by Duhem with having carried out “the most important researches on that subject”: F. Massieu, J.W. Gibbs, H. von Helmholtz, and A. von Oettingen. If Massieu had managed to derive Thermodynamics from a “characteristic function and its partial derivatives”, Gibbs had shown that Massieu’s functions “could play the role of potentials in the determination of the states of equilibrium” in a given system. If Helmholtz had put forward “similar ideas”, Oettingen had given “an exposition of Thermodynamics of remarkable generality”. Duhem did not claim that he would have done “better” than the scientists quoted above, but he thought that there was real “interest” in putting forward “the analytic development of the mechanical Theory of heat”, making recourse to “very different methods”.<sup>84</sup>

In the first section, “Etude thermique d’un système dont on se donne les équations d’équilibre”, he took into account a system whose elements had the same temperature: the state of the system could be completely specified by giving its temperature  $\vartheta$  and  $n$  other independent quantities  $\alpha, \beta, \dots, \lambda$ . He then introduced some “external forces”, which depended on  $\alpha, \beta, \dots, \lambda$  and  $\vartheta$ , and held the system in equilibrium. A virtual work  $d\tau_e = A \cdot \delta\alpha + B \cdot \delta\beta + \dots + L \cdot \delta\lambda + \Theta \cdot \delta\vartheta$  corresponded to such forces, and a set of  $n+1$  equations corresponded to the condition of equilibrium of the physical system:

$$\begin{aligned} A &= f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta) \\ B &= f_\beta(\alpha, \beta, \dots, \lambda, \vartheta) \\ &\dots \\ L &= f_\lambda(\alpha, \beta, \dots, \lambda, \vartheta) \\ \Theta &= f_\vartheta(\alpha, \beta, \dots, \lambda, \vartheta). \end{aligned} \quad ^{85}$$

From the thermodynamic point of view, every infinitesimal transformation involving the generalized *displacements*  $\delta\alpha, \delta\beta, \dots, \delta\lambda$  and  $\delta\vartheta$  had to obey to the first law  $dQ = -dU + (1/E)d\tau_e$ , which could be expressed in terms of the  $(n+1)$  generalised Lagrangian parameters:

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<sup>83</sup> Duhem P. 1886, pp. 9-10.

<sup>84</sup> Duhem P. 1891, pp. 231-2. Duhem specified that the paper stemmed from his activity as a lecturer “de la Faculté de Sciences de Lille”. See *Ibidem*, p. 232. From the Duhem theoretical context it is clear that the expression “mechanical Theory of heat” cannot be interpreted in the same sense as Maxwell and Boltzmann.

<sup>85</sup> Duhem P. 1891, p. 233-4.



$$dQ = -\left(\frac{\partial U}{\partial \alpha} \cdot \delta\alpha + \frac{\partial U}{\partial \beta} \cdot \delta\beta + \dots \frac{\partial U}{\partial \lambda} \cdot \delta\lambda + \frac{\partial U}{\partial \vartheta} \cdot \delta\vartheta\right) + \frac{1}{E} (A \cdot \delta\alpha + B \cdot \delta\beta + \dots L \cdot \delta\lambda + \Theta \cdot \delta\vartheta).$$

The amount of heat could be written as a sum of  $(n+1)$  terms:

$$dQ = -\left[\left(\frac{\partial U}{\partial \alpha} - \frac{A}{E}\right) \cdot \delta\alpha + \left(\frac{\partial U}{\partial \beta} - \frac{B}{E}\right) \cdot \delta\beta + \dots \left(\frac{\partial U}{\partial \lambda} - \frac{L}{E}\right) \cdot \delta\lambda + \left(\frac{\partial U}{\partial \vartheta} - \frac{\Theta}{E}\right) \cdot \delta\vartheta\right], \text{ or}$$

$$dQ = -\left[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta\right],$$

wherein

$$R_\alpha = \frac{\partial U}{\partial \alpha} - \frac{A}{E}, \quad R_\beta = \frac{\partial U}{\partial \beta} - \frac{B}{E}, \quad \dots \dots, \quad R_\lambda = \frac{\partial U}{\partial \lambda} - \frac{L}{E}, \quad R_\vartheta = \frac{\partial U}{\partial \vartheta} - \frac{\Theta}{E}.$$

The alliance between Mechanics and Thermodynamics led to a sort of symmetry between thermal and mechanical quantities. The  $n+1$  functions  $R_\alpha, R_\beta, \dots, R_\lambda, R_\vartheta$ , which Duhem re-wrote as  $R_\alpha, R_\beta, \dots, R_\lambda, C$ , played the role of *generalized thermal capacities*, and the last term  $C$  was nothing else but the ordinary thermal capacity: in some way, the second typographical choice re-established the traditional asymmetry.<sup>86</sup>

In the following pages Duhem inquired into the connection between the mathematical and physical aspects of the principle of equivalence. Starting from the first and second Principles of Thermodynamics, he arrived at the equations

$$\frac{\partial R_\alpha}{\partial \beta} - \frac{\partial R_\beta}{\partial \alpha} = -\frac{1}{E} \left( \frac{\partial A}{\partial \beta} - \frac{\partial B}{\partial \alpha} \right)$$

$$\frac{\partial R_\alpha}{\partial \vartheta} - \frac{\partial C}{\partial \alpha} = -\frac{1}{E} \left( \frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right).$$

He stressed the relationship between mathematical and physical *equivalences*. The physical *equivalence* between work and heat corresponded to a mathematical *equivalence* between their  $n+1$  differential coefficients  $A, B, \dots, L, \Theta$ , and  $R_\alpha, R_\beta, \dots, R_\lambda$ . In its turn, the mathematical equivalence expressed by the last equations required the existence of a function of state  $U$ , namely “a uniform function of  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ , so that  $E(dQ + dU) = d\tau_e$ ”.<sup>87</sup>

The Lagrangian parameter  $\vartheta$  could be chosen without any restriction: it did not have to be necessarily identified with the absolute temperature. In general, the absolute temperature could be a function  $F(\vartheta)$  of  $\vartheta$ . This means that the function entropy, a “uniform, finite, and continuous function of  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ ”, could be defined as

<sup>86</sup> Duhem P. 1891, p. 234.

<sup>87</sup> Duhem P. 1891, p. 235.

$$dS = \frac{dQ}{F(\vartheta)} = \frac{-[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta]}{F(\vartheta)} =$$

$$-\frac{R_\alpha}{F(\vartheta)} \cdot \delta\alpha - \frac{R_\beta}{F(\vartheta)} \cdot \delta\beta - \dots - \frac{R_\lambda}{F(\vartheta)} \cdot \delta\lambda - \frac{R_\vartheta}{F(\vartheta)} \cdot \delta\vartheta.$$

New mathematical equivalences could be derived:

$$\frac{\partial}{\partial\beta} \frac{R_\alpha}{F(\vartheta)} = \frac{\partial}{\partial\alpha} \frac{R_\beta}{F(\vartheta)}, \text{ or } \frac{1}{F(\vartheta)} \left( \frac{\partial R_\alpha}{\partial\beta} - \frac{\partial R_\beta}{\partial\alpha} \right) = 0,$$

$$\frac{1}{F(\vartheta)} \left( \frac{\partial R_\alpha}{\partial\vartheta} - \frac{F'(\vartheta)}{F(\vartheta)} R_\alpha \right) = \frac{1}{F(\vartheta)} \frac{\partial C}{\partial\alpha}.^{88}$$

Even in this case, the mathematical and physical steps could be reversed. The mathematical equivalence expressed by the last equations required the existence of a function of state  $S$ , namely “a uniform function  $S$  of the state of the system”  $dS = dQ/F(\vartheta)$ . In the context of the generalised theory, the functions internal energy  $U$  and entropy  $S$  also emerged as two basic state-functions.<sup>89</sup>

The above mentioned mathematical equivalences had an important consequence from both the mathematical and physical points of view. In fact, they led to a series of equations of the kind

$$\frac{\partial A}{\partial\beta} - \frac{\partial B}{\partial\alpha} = 0.$$

As Duhem remarked, this equation says that the  $n+1$  differential coefficients  $A, B, \dots, L$ , and  $\Theta$ , “cannot be chosen arbitrarily”. In particular it suggests that “a uniform, finite, and continuous function  $\mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta)$  of  $n+1$  parameters  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$  there exist”. The gradient of  $\mathcal{F}$  can be written component by component, taking care of the specific behaviour of the component  $\Theta$ , which was “independent of the function  $\mathcal{F}$ ”:

$$A = \frac{\partial}{\partial\alpha} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta), B = \frac{\partial}{\partial\beta} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta), \dots L = \frac{\partial}{\partial\lambda} \mathcal{F}(\alpha, \beta, \dots, \lambda, \vartheta).^{90}$$

<sup>88</sup> Duhem P. 1891, pp. 235-6. Here a sort of asymmetry between *mechanical* and *thermal* parameters emerges.

<sup>89</sup> Duhem P. 1891, p. 236. Duhem acknowledged that his mathematical and physical approach had already been outlined by Clausius, Kirchhoff, and Reech in the 1850s and 1860s. See *Ibidem*, p. 237.

<sup>90</sup> Duhem P. 1891, pp. 237-8.

What do we know about the functions  $\Theta$  and  $R_{\vartheta} = C$ , which could not be derived by the same procedure? The knowledge of the “equilibrium equations of a system” allowed Duhem to compute the partial derivatives of the thermal capacity  $C$  with regard to all the parameters which described the state of the system, “apart from its derivative with regard to temperature”. The thermal capacities were therefore known “except for an unspecified function of temperature”:

$$(9) \quad \frac{\partial C}{\partial \alpha} = \frac{1}{E} \left\{ \left( \frac{\partial A}{\partial \vartheta} - \frac{\partial \Theta}{\partial \alpha} \right) \left[ 1 - \frac{\partial F(\vartheta)}{\partial \vartheta F'(\vartheta)} \right] - \frac{F(\vartheta)}{F'(\vartheta)} \left( \frac{\partial^2 A}{\partial \vartheta^2} - \frac{\partial^2 \Theta}{\partial \alpha \partial \vartheta} \right) \right\},$$

$$\frac{\partial C}{\partial \beta} = \dots, \dots, \quad \frac{\partial C}{\partial \lambda} = \dots$$

The last set of equations shows how deeply entangled were the *thermal* and *mechanical* properties of a physical system.<sup>91</sup>

The complex net of equations developed by Duhem could be simplified by an appropriate choice of Lagrangian parameters: the choice of the absolute temperature as thermal parameter, namely  $\vartheta = T$  and  $F(T) = T$ , let simpler expressions for  $C$  derivatives emerge. A further simplification could be attained by choosing the parameters  $\alpha$ ,  $\beta$ , ..., and  $\lambda$  in order to keep at rest the whole system when the parameter  $\vartheta$  changed. In this case, “the mere change of  $\vartheta$  cannot involve any work done by external forces”, and a sort of split between thermal and mechanical features of the system was imposed. Nevertheless, the existence of mathematical links between the *mechanical* derivatives of the *thermal* scalar  $C$  and the *thermal* derivatives of the generalised *mechanical* vector ( $A$ ,  $B$ , ...,  $L$ ) shows us the persistence of the deep connection between mechanical and thermal effects, even when the formal symmetry between them was weakened:

$$\frac{\partial C}{\partial \alpha} = -\frac{T}{E} \frac{\partial^2 A}{\partial T^2}, \quad \frac{\partial C}{\partial \beta} = -\frac{T}{E} \frac{\partial^2 B}{\partial T^2}, \dots, \dots, \quad \frac{\partial C}{\partial \lambda} = -\frac{T}{E} \frac{\partial^2 L}{\partial T^2}.$$

According to Duhem, “the mechanical determination of the system” required firstly the specification of the function  $\mathcal{F}$ , and then the deduction of the generalized forces  $A$ ,  $B$ , ...,  $L$ , and  $\Theta$ , and the “thermal coefficients”  $R_{\alpha}$ ,  $R_{\beta}$ , ..., and  $R_{\lambda}$ . Duhem’s vocabulary swung freely between the mechanical and the thermal poles: the fact is that both the series of generalized forces and generalized thermal coefficients had *mechanical* and *thermal* meaning. He thought that, from the formal point of view, he had really perfected the design outlined in 1886: the derivation of mechanical and thermal features of the system from the potential  $\mathcal{F}$  and the function  $\Theta$ .<sup>93</sup>

<sup>91</sup> Duhem P. 1891, pp. 238-9.

<sup>92</sup> Duhem P. 1891, pp. 239-41.

<sup>93</sup> Duhem P. 1891, p. 251. An unaccountable missing sign in the equation for entropy led Duhem to compute, in a relatively easy way, the expressions for  $U$ ,  $S$  and  $C$ . The fact is that the mistaken sign makes the derivation too easy: the right computation leads to differential equations for  $U$  and  $S$ , which are not so easy to solve. The

In 1892 Duhem submitted a long paper with the very general title “Commentaires aux principes de la Thermodynamique” to the *Journal de mathématiques pures et appliquées*. It was the first part of a sort of trilogy whose second and third parts were hosted by the *mathematical* journal in 1893 and 1894 respectively. The set of three papers, when considered as a whole, was nothing less than a treatise on thermodynamics.

He pointed out the difference between the physical quantities which preserved their values over time, and those which did not: mass and electric charge belonged to the first set, while kinematical parameters belonged to the second one. He qualified the former as those which “define the nature of the system”, and the latter as those which “define the state”: he labelled  $A, B, \dots$ , and  $L$  the elements of the first set, and  $\alpha, \beta, \dots$ , and  $\lambda$  the elements of the second. Matter could be described geometrically by some functions of Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ : among state quantities Duhem distinguished those which appeared explicitly in those equations from those which did not appear. He reserved the labels  $\alpha, \beta, \dots$ , and  $\lambda$  for the former, and introduced new labels  $a, b, \dots, l$  for the latter: in some way he separated geometrical quantities from other quantities. In the latter subset Duhem placed temperature, a quantity which would have played “a remarkable role in the present work”. According to Duhem, temperature was not a “quantitative feature” of a physical system: a given value of temperature could be “reproduced, increased and decreased”, but temperature did not have the additive property. Temperature could not *measure* literally, but only *locate* the different levels of heat. Moreover, temperature could not be univocally defined: after having defined a temperature  $\vartheta$ , any continuous and increasing function  $\Theta = f(\vartheta)$  could play the role of temperature.<sup>94</sup>

In the third chapter he started from a complex system  $\Sigma$ , which was isolated in space, and could be looked upon as the composition of two “independent systems”  $S$  and  $S'$ . If the kinetic energy of  $\Sigma$  was simply the sum of the kinetic energies  $\mathcal{T}$  and  $\mathcal{T}'$  of  $S$  and  $S'$ , the potential energy could not consist only of the sum of the two isolated potential energies  $U$  and  $U'$ , but had to contain a term of *interaction*:

$$Y = U(\alpha, \beta, \dots, \lambda; a, b, \dots, l) + U'(\alpha', \beta', \dots, \lambda'; a', b', \dots, l') \\ + \Psi(\alpha, \beta, \dots, \lambda; a, b, \dots, l; \alpha', \beta', \dots, \lambda'; a', b', \dots, l')$$

The key entity was the total energy

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qualitative features of Duhem’s design are not threatened by the wrong derivation, and its conclusion is qualitatively correct. Duhem’s mistake stems from the difference between the definition  $dQ/F(\vartheta) = dS$  (p. 236) and the other definition  $\delta S = -dQ/F(\vartheta)$  (p. 251).

<sup>94</sup> Duhem 1892, pp. 276, 278-9, 284 and 286-8. According to Duhem, temperature stemmed from the concept of “equally warm”, and could replace that concept in the definition of equilibrium: “if an isolated system is in equilibrium, the temperature  $\vartheta$  has the same value everywhere”. In the second chapter, he tried to clarify some basic physical concepts: closed cycle, work, kinetic and potential energies, internal energy, the additive property of work, and the principle of the conservation of energy. He stressed the status of “physical hypothesis” of that principle: it was submitted to experience, and it could not be demonstrated, but only put forward by means of some physical considerations. (*Ibidem*, pp. 291-307)

$$\varepsilon = Y + \frac{1}{E}(\mathcal{T} + \mathcal{T}') = U + U' + \Psi + \frac{1}{E}(\mathcal{T} + \mathcal{T}').$$

Heat had a relational nature: in a “complex isolated system, consisting of two independent systems S and S’, ... one of them sends out as much heat as the other receives”. The concept of an isolated body placed in an empty space, and sending out or receiving heat, seemed to Duhem “not consistent with the definition given above”. According to Duhem, heat meant exchange of heat: heat required interactions between different bodies, or at least between a body and the surrounding aether.<sup>95</sup>

Consistently with the separation between geometrical and “state” parameters, he introduced two sets of “thermal coefficients”,  $R_\alpha, R_\beta, \dots, R_\lambda$ , and  $\mathcal{R}_a, \mathcal{R}_b, \dots, \mathcal{R}_l$ , such that

$$E R_\alpha = \left( E \frac{\partial U}{\partial \alpha} - A \right) - \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right), \quad E R_\beta = \dots, \quad E R_\lambda = \dots$$

$$E \mathcal{R}_a = \left( E \frac{\partial U}{\partial a} - \mathcal{A} \right), \quad E \mathcal{R}_b = \dots, \quad E \mathcal{R}_l = \dots$$

$$dQ = - \left[ (R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots + R_\lambda \cdot \delta\lambda) + (\mathcal{R}_a \cdot \delta a + \mathcal{R}_b \cdot \delta b + \dots + \mathcal{R}_l \cdot \delta l) \right].$$

In the first set of equations, geometrical parameters involved the motion of the physical system as a whole, and ordinary Lagrangian terms appeared. On the right-hand side of the last equation, the first round brackets contained the effect of mechanical actions, and the second the effects of other kinds of *influences*: the latter was a generalization of the term  $R_\theta$  which Duhem had introduced in 1891. Virtual work was the sum of three components, since actions split into *forces* and *influences*:  $d\tau = d\tau_1 + d\tau_2 + d\tau_3$ , where

$$d\tau_1 = (A \cdot \delta\alpha + \dots), \quad d\tau_2 = (\mathcal{A} \cdot \delta a + \dots), \quad d\tau_3 = \left[ \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) \delta\alpha + \dots \right].<sup>96</sup>$$

Duhem’s generalised Mechanics/Thermodynamics became a sort of Analytical Thermodynamics, and ordinary mechanics could be looked upon as one of its specific implementations. In order to derive ordinary mechanics from his thermodynamics, he assumed that  $dQ=0$ , and all “thermal coefficients” vanished. In this case, the equations became

<sup>95</sup> Duhem 1892, pp. 308-10 and 319-20. In the last part of the chapter, Duhem stressed his relational conception of heat once again. See p. 323: “Ici vient naturellement se placer une réflexion semblable à celle que nous a suggérée la définition du travail : on ne peut parler de la quantité de chaleur dégagée par chacune des parties d’un système qu’autant que chacune de ces parties peut être considérée comme un système indépendant. Lorsque les diverses parties d’un système ne sont pas indépendantes les unes des autres, le mot : quantité de chaleur dégagée par chacune d’elles n’a aucun sens.”

<sup>96</sup> Duhem 1892, pp. 320-1.

$$\left( E \frac{\partial U}{\partial \alpha} - A \right) - \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) = 0, \dots \dots,$$

$$E \frac{\partial U}{\partial \alpha} - \mathcal{A} = 0, \dots \dots$$

Since the first set of equations corresponded to Lagrange's equations of rational mechanics, the derivation seemed successfully achieved. Nevertheless, a question arose: could the physical derivation be reversed? In other words, are we sure that, when ordinary mechanics is at stake, all thermal coefficients vanish? At that stage, Duhem could not satisfactorily answer the question, and he acknowledged that further theoretical investigations were required. At the end of Duhem's 1892 paper, the nature of the formal relationship between Mechanics and Thermodynamics was waiting for a complete clarification.<sup>97</sup>

In 1894, in the third part of his *Commentaire*, he astonished the readers because of the reference to an Aristotelian interpretation of the word "motion": not only was motion looked upon as a kinematic process, but as transformation in general. It is worth quoting Duhem's whole passage.

Nous prenons, dans ce Chapitre, le mot *mouvement* pour désigner non seulement un changement de position dans l'espace, mais encore un changement d'état quelconque, lors même qu'il ne serait accompagné d'aucun déplacement. Ainsi, il y aurait mouvement si les variables que nous avons désignées par  $a, b, \dots, l \dots$  variaient seules, les variables  $\alpha, \beta, \dots, \lambda$  gardant des valeurs fixes. De la sorte, le mot *mouvement* s'oppose non pas au mot *repos*, mais au mot *équilibre*.<sup>98</sup>

Then he opened another pathway: instead of starting from general equations, he started from the case of thermal equilibrium ( $dQ=0$ ), which corresponded to the specific mechanical instance, and introduced a perturbation, which represented a source of irreversibility for the physical system:

$$A' - \frac{\partial \mathcal{F}}{\partial \alpha} + \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \alpha'} \right) = -f_\alpha, \dots \dots, L' - \frac{\partial \mathcal{F}}{\partial \lambda} + \left( \frac{\partial \mathcal{T}}{\partial \lambda} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial \lambda'} \right) = -f_\lambda.$$

The new functions  $f_\alpha, f_\beta, \dots, f_\lambda$  represented "passive resistances to be overcome by the system". Those resistances depended on basic parameters  $\alpha, \beta, \dots, \lambda, \vartheta$ , their time derivatives  $\alpha', \beta', \dots, \lambda'$ , and time  $t$ : from the mathematical point of view, they were "resistances" in the usual mechanical sense. Equilibrium was *perturbed* by actions which were the generalisation of mechanical *friction*: the total work  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$  could be associated to that kind of actions. Once again, for his generalized thermodynamics,

<sup>97</sup> See Duhem P. 1892, p. 324: "On voit que les lois de la Dynamique rentrent, comme cas particulier, dans les lois de la Thermodynamique ; elles se déduisent de ces dernières en supposant tous les coefficients calorifiques du système égaux à 0 ; mais dans quel cas cette hypothèse est-elle vérifiée? C'est une question qui reste à examiner et que rien, dans ce que nous avons dit jusqu'ici, ne permet de résoudre. Dans la plupart des cas, elle n'est résolue que par voie d'hypothèse, directe ou indirecte. D'ailleurs, nous verrons plus tard qu'il existe une autre manière, distincte de celle-là, de faire dériver les équations de la Dynamique des équations de la Thermodynamique."

<sup>98</sup> Duhem P. 1894, p. 222.

Duhem chose a generalisation of the traditional mechanical lexicon. He was transforming the meaning of mechanical concepts and words, in order to set up a new generalized and Aristotle-flavoured physics.<sup>99</sup>

Unfortunately the last  $n$  equations depended on the  $n+1$  Lagrangian parameters  $\alpha, \beta, \dots, \lambda$ , and  $\vartheta$ , and Duhem did not have at his disposal a mechanical generalization for the equation corresponding to the parameter  $\vartheta$ .

Lorsque l'état des corps extérieurs est donné à chaque instant  $t$ , les résistances passives deviennent des fonctions des variables

$$\alpha, \beta, \dots, \lambda, \vartheta, \alpha', \beta', \dots, \lambda', t.$$

Les équations ... deviennent lors des équations différentielles du second ordre, qui détermineraient les valeurs des variables  $\alpha, \beta, \dots, \lambda, \vartheta$ , en fonction de  $t$ , et, partant, le mouvement du système, si elles étaient en nombre suffisant ; *mais le nombre des variables dont il faut déterminer la valeur à chaque instant excède d'une unité le nombre des équations du mouvement fournies par la Thermodynamique* ; il faudra donc, pour compléter la mise en équations du problème, emprunter une dernière équation à une théorie physique étrangère à la Thermodynamique ; telle serait, par exemple, l'équation

$$\vartheta = \varphi(t)$$

qui ferait connaître à chaque instant la température du système.<sup>100</sup>

Duhem was forced to look for the missing equation outside the field of his formal structure: purely thermal processes, involving only temperature changes over time, could not naturally emerge from his theoretical generalisation. Nevertheless, he dared to widen the formal structure of the “thermal coefficients” he had introduced in 1891, and had subsequently generalized in the first Part of his *Commentaire*. The updated version was only slightly different, since it contained the generalized resistances:

$$E R'_\alpha = \left( E \frac{\partial U}{\partial \alpha} - A' \right) - \left( \frac{\partial \mathcal{T}}{\partial \alpha} - \frac{d}{dt} \frac{\partial \mathcal{T}}{\partial u} \right) + f_\alpha, \dots, \dots$$

In the  $\vartheta$ -component of this series of equations, the term representing the passive resistance was missing: it had not been put forward at the beginning, and it could not be found at the end.<sup>101</sup>

Consistently with the conceptual framework of a generalized Mechanics, he put forward a “fundamental hypothesis” on the passive *resistances*  $f_\alpha, f_\beta, \dots, f_\lambda$ : the work done by them could be only null or negative. That hypothesis allowed Duhem to attain a meaningful result concerning the second Principle of Thermodynamics. If in 1891

<sup>99</sup> Duhem P. 1894, pp. 223-4. In this case the symbolic mismatch seems even more puzzling: in 1891 Duhem had made use of the functions  $f_\alpha, f_\beta, \dots, f_\lambda$  in order to express explicitly the dependence of external forces on the basic parameters, namely  $A = f_\alpha(\alpha, \beta, \dots, \lambda, \vartheta)$  and so on. In 1894, the new *dissipative forces*  $f_\alpha, f_\beta, \dots, f_\lambda$  had to be added to the already existing forces  $A', B', \dots, L'$ .

<sup>100</sup> Duhem P. 1894, pp. 224-5.

<sup>101</sup> Duhem P. 1894, pp. 225-6.

$$dS = \frac{dQ}{F(\vartheta)} = \frac{-[R_\alpha \cdot \delta\alpha + R_\beta \cdot \delta\beta + \dots R_\lambda \cdot \delta\lambda + R_\vartheta \cdot \delta\vartheta]}{F(\vartheta)},$$

in 1894

$$\begin{aligned} \frac{dQ}{F(\vartheta)} &= \frac{-[R'_\alpha \cdot \delta\alpha + \dots R'_\lambda \cdot \delta\lambda + C \cdot \delta\vartheta]}{E F(\vartheta)} \\ &= -dS - \frac{f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda}{E F(\vartheta)}. \end{aligned}$$

For a closed cycle,  $\int dS = 0$ , and therefore

$$\int \frac{dQ}{F(\vartheta)} = - \int \frac{f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda}{E F(\vartheta)}.$$

If  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda \leq 0$ , then  $\int \frac{dQ}{F(\vartheta)} \geq 0$ .

Duhem could finally identify the work  $f_\alpha \cdot d\alpha + f_\beta \cdot d\beta + \dots + f_\lambda \cdot d\lambda$  with Clausius' "uncompensated work".<sup>102</sup>

Generalised resistances allowed Duhem to re-interpret entropy: in an isolated system,  $dQ=0$ , and

$$dS = - \frac{f_\alpha \cdot d\alpha + \dots + f_\lambda \cdot d\lambda}{E F(\vartheta)}.$$

Because of the positive value of the right-hand side of the equation, the left-hand side, namely entropy, was positive as well: no transformation in isolated systems could "make the entropy of the system increase".<sup>103</sup>

The concept of thermal dissipation in natural phenomena was mathematically dressed with the clothes of mechanical dissipation. The second principle of Thermodynamics had therefore received a mechanical interpretation, but that interpretation was mechanical in a sense to be carefully specified. As I have already stressed, we are not dealing here with a microscopic mechanical explanation of macroscopic thermodynamic effects. We find a macroscopic

<sup>102</sup> Duhem P. 1894, pp. 228-9.

<sup>103</sup> Duhem P. 1894, p. 229.



mechanical re-interpretation, linked to a re-interpretation of the word “motion” in a new Aristotelian perspective.

At the end of the third Part of his *Commentaire*, Duhem outlined some general “Conclusions”, where he put his approach to Mechanics and Thermodynamics into a historical perspective. He identified two different pathways to Thermodynamics. On the one hand, most of the founding fathers of Thermodynamics had tried to transform Thermodynamics into “an application of Dynamics”. They had interpreted heat as “the microscopic and very fast motion of particles which form ordinary bodies”, and temperature as the “average living force” corresponding to those motions. On the other hand, other physicists had tried to found Thermodynamics “on its own principles”. They had not put forward “hypotheses on the nature of heat”; neither had they “borrowed theorems from rational Mechanics”. The former had managed to successfully interpret the first Principle, namely the Principle of conservation of energy, but had failed to explain the second Principle or “Carnot’s Principle”. In spite of their “daring efforts”, Clausius, Boltzmann and Helmholtz “had not managed to make Carnot’s principle stem from the laws of Dynamics in a satisfactory way”. According to Duhem, the latter had attained more success.<sup>104</sup>

He claimed that he had undertaken a third pathway: Thermodynamics as a wide-scope theory of transformations. His design can be looked upon as a reduction of physics to the language of Analytical Mechanics, but at the same time, as an anti-reductionist design, which involved a deep re-interpretation of that language. In Duhem’s “more general science” we find the coexistence of a mechanical approach, in the sense of Lagrange’s mathematical physics, and the rejection of “a mechanical explication of the Universe”, in the sense of specific mechanical devices.<sup>105</sup>

From the 1880s onwards, Duhem had pursued a new alliance between Lagrangian mechanics and the science of heat, and that pursuit was not an isolated enterprise. In the same years, in Great Britain, G.F. FitzGerald, J.J. Thomson and J. Larmor were looking for a new alliance between Lagrangian mechanics and the science of electromagnetic phenomena. A new kind of alliance between abstract Mechanics and a field theory purified by the concept of force led Hertz to a bold design of the geometrization of physics in 1894.<sup>106</sup>

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<sup>104</sup> Duhem P. 1894, pp. 284-5.

<sup>105</sup> See Duhem P. 1894, p. 285: “Nous avons essayé, dans le présent travail, d’indiquer une troisième position de la Dynamique par rapport à la Thermodynamique ; nous avons fait de la Dynamique un cas particulier de la Thermodynamique, ou plutôt, nous avons constitué sous le nom de Thermodynamique, une science qui embrasse dans des principes communs tous les changements d’état des corps, aussi bien les changements de lieu que les changements de qualités physiques [...]; on comprendra mieux que le changement de lieu dans l’espace n’est pas une modification plus simple que le changement de température ou de quelque autre qualité physique ; on fuira dès lors plus volontiers ce qui a été jusqu’ici le plus dangereux écueil de la Physique théorique, la recherche d’une explication mécanique de l’Univers.”

<sup>106</sup> Hertz’s main aim was the reduction of all physics to a generalised new mechanics. Fundamental laws and concepts of mechanics had to be clarified, in order to rebuild a reliable theoretical framework, where “the ideas of force and the other fundamental ideas of mechanics appear stripped of the last remnant of obscurity”. In the end, physics was reduced to mechanics and mechanics was reduced to geometry and kinematics. This new physics appeared in accordance with the theoretical model of contiguous action. See Hertz H. 1894, in Hertz H. 1956, “Author’s Preface”, p. 1, and p. 41.

### Concluding remarks

In the last decades of the XIX century we find in front of us two kinds of Mechanics: mechanics as mechanical models and machinery on the one hand, and mechanics as a formal language for physical sciences, on the other. If something like “the crisis of Mechanics” crossed the late XIX century, it did not dwell at Massieu, Gibbs, Helmholtz, Planck, Oettingen, and Duhem’s homes, because they were not involved in devising tangled machinery of matter and aether.

Duhem put forward the most original and systematic reinterpretation of Thermodynamics, and at the same time the boldest upgrade of Analytical Mechanics. In 1896, in the very long essay “Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques”, he made a detailed reconstruction of some physical and chemical processes neglected or underestimated by physicists because of their complexity. In the equations of his generalized Mechanics-Thermodynamics, the collection of physical parameters contained geometrical variables, temperature, and chemical concentrations. New terms had to be introduced in the generalised equations of motions, in order to account for complex chemical reactions.

In 1901 Duhem synthesised his theoretical pathway in the *Revue des questions scientifiques*, and interpreted that pathway as an improvement or “evolution” of Mechanics. It is worth stressing that what in 1894 he had qualified as a third pathway to Thermodynamics, in 1901 was looked upon as an evolution of Mechanics. He had contributed to widen the scope of Mechanics, and at the same time, he had contributed to lead Mechanics beyond the boundaries of “local motion”. According to Duhem, the old mechanical world-view was a “daring pathway”, where non-geometrical features of physical systems were forced to be expressed in geometrical terms, but the attempt to reduce thermal and electric phenomena to matter and motion had led to “overwhelming difficulties”.<sup>107</sup>

He claimed to have undertaken a “larger and safer pathway”, where all states and features of a physical system were accepted without any reduction to matter and motion. They could be translated into Lagrangian parameters: as a consequence traditional rational Mechanics became “nothing more than the first chapter “ of a more general Mechanics. In other words, local motion became only a section of a “science” dealing with “every kind of change of state and quality”.<sup>108</sup>

The principle of virtual velocities of “the ancient Statics” acquired “a wider meaning”, and was expressed by the equation

$$dT_e - dF = 0,$$

where the first symbol represented the infinitesimal work of external actions, and the second represented Gibbs’ “*internal thermodynamic potential*” of the physical system.<sup>109</sup>

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<sup>107</sup> Duhem P. 1901, pp. 130-1.

<sup>108</sup> Duhem P. 1901, pp. 131-3.

<sup>109</sup> Duhem P. 1901, pp. 131-3.

When the work performed by “inertial forces”  $dT_j$  and “the virtual work of viscosity”  $dT_v$  were taken into account, the equation became

$$dT_e + dT_j + dT_v - dF = 0,$$

where the word “viscosity” represented a generalisation of the old mechanical meaning.

If  $dT_j = J_\alpha d\alpha + J_\beta d\beta + \dots + J_\lambda d\lambda$  and  $dT_v = V_\alpha d\alpha + V_\beta d\beta + \dots + V_\lambda d\lambda$ , the generalised equations of motion became

$$A - \frac{\partial F}{\partial \alpha} + J_\alpha + V_\alpha = 0.$$

$$B - \frac{\partial F}{\partial \beta} + J_\beta + V_\beta = 0$$

... ..

$$L - \frac{\partial F}{\partial \lambda} + J_\lambda + V_\lambda = 0.^{110}$$

In 1896 the generalisation of the concept of mechanical “friction” and mechanical “hysteresis” had led to even more general equations where  $\alpha' = d\alpha/dt$ :

$$A - \frac{\partial F}{\partial \alpha} + J_\alpha + V_\alpha + F_\alpha \frac{\alpha'}{|\alpha'|} = 0.$$

$$B - \frac{\partial F}{\partial \beta} + J_\beta + V_\beta + F_\beta \frac{\beta'}{|\beta'|} = 0$$

... ..

$$L - \frac{\partial F}{\partial \lambda} + J_\lambda + V_\lambda + F_\lambda \frac{\lambda'}{|\lambda'|} = 0,$$

This mechanical approach, on the track of Analytical Mechanics, offered a consistent interpretation of the second principle of Thermodynamics. In case of cyclical transformations without any dissipation,

$$\oint \frac{dQ}{T} = 0,$$

whereas dissipative effects like generalised viscosities, frictions and hysteresis led to

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<sup>110</sup> Duhem P. 1901, pp. 136, 139, and 145.

$$\oint \frac{dQ}{T} > 0.^{111}$$

Duhem was aware that, along his pathway, the words and the mathematical structures of Mechanics experienced a bold generalisation and re-interpretation, in order to express a series of phenomena which lay outside the traditional boundaries of Mechanics. In this sense, Duhem's programme of research was anti-mechanical, because he refused the reduction of non-mechanical features to matter and *local* motions at the microscopic level. At the same time, his programme was *mechanical* in a wider sense, because he aimed at widening the boundaries and the scope of Analytical Mechanics. In other words, Rational Mechanics offered the formal structure or the formal language for physics, even for the fields of physics which did not deal with mechanics. The language of rational mechanics had nothing to do with the specific mechanical models which had been used by some physicists in the context of Thermodynamics.

Duhem's design had a two-fold target: the unification of physics under the principles of thermodynamics, and the translation of that unified physics into a sophisticated mathematical language. The specific features of Duhem's design were quite different from the specific features of Boltzmann's design: if the latter had tried to give a microscopic mechanical explanation of the macroscopic laws of Thermodynamics, Duhem assumed those macroscopic laws as starting point. There is a great difference between their theoretical procedures indeed, even though we cannot find a great difference in their general perspectives. Both Boltzmann and Duhem exploited the tradition in which they had been trained, and led it to its ultimate consequences; at the same time, they dared to go far beyond that tradition.

In the second edition (1984) of his book *Rational Thermodynamics*, Clifford A. Truesdell regretted that "DUHEM's work had fallen into the general oblivion of classical mechanics in the interbellum", although "most of the work since 1960" had followed "the example of DUHEM". He recommended that "DUHEM's researches be studied until justice be done them", and qualified Duhem's Preface to his *Treatise on Energetics or General Thermodynamics* as a "program of modern rational thermodynamics".<sup>112</sup>

Truesdell remarked that, before Duhem, Thermodynamics had fluctuated between technology and cosmology: he saw the interpretation of thermal engines, on the one hand, and "the speculations about the universe", on the other. Thermodynamics had "always had a hard time striking a mean between these extremes": while "its claims" had often been "grandiose", its applications are usually trivial". Furthermore, the mathematics of thermodynamics appeared to Truesdell obscure and misleading. He aimed to state and teach Thermodynamics "just as classical mechanics is stated precisely and learned". Truesdell's aim was not different from Duhem's: in Truesdell's words, he was himself looking for "a thermodynamic theory formally similar to the classical one but vastly more general in scope". Generalized Thermodynamics should "extend the concepts of mechanics so as to allow for diffusion and chemical reactions as well".<sup>113</sup>

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<sup>111</sup> Duhem P. 1901, pp. 145-6, 153, and 155-6.

<sup>112</sup> Truesdell C. 1984, p. 38, 40-1 and 45.

<sup>113</sup> Truesdell C. 1984, pp. 59, 61-2, and 106. With regard to mathematics, he regretted that the readers of textbooks on Thermodynamics had to face equations like  $T \cdot dS \geq \delta Q$ . See p. 61: "He is told that  $dS$  is a differential, but not of what variables  $S$  is a function; that  $\delta Q$  is a small quantity not generally a differential; he is

What Truesdell called “modern continuum thermodynamics” consisted of a “collection” of theories concerning “elastic materials”, “viscous materials”, “materials with memory”, “mixtures”, and so on. Nevertheless, all these branches of physics were based on the same principle: the “Clausius-Duhem inequality”. In brief, “*for any process suffered by any body composed of the material under study*”, Rational Thermodynamics assumed

$$S - S_0 \geq \int \frac{dq}{\vartheta} \Big|_{process},$$

“*dq denoting the element of heat received from external sources and  $\vartheta$  the temperature of the part of the system receiving it*”. Truesdell claimed that this inequality could be applied to “general motions”, far beyond the states of equilibrium: to deny this was to deny “that there can be such a thing as a thermodynamics of irreversible processes”.<sup>114</sup>

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expected to believe not only that a differential can be bigger than another, but even that a differential can be bigger than something which is not a differential.”

<sup>114</sup> Truesdell C. 1984, pp. 123 and 157. The *Clausius-Duhem* inequality was explicitly mentioned by Truesdell for the first time in 1960, in the long essay “The Classical Field Theories” he published in 1960 together with Richard Toupin. (I thank Sandro Caparrini for this information.) In the second half of the twentieth century, other mathematical physicists developed what we call rational thermodynamics: among them, Bernard Coleman and Walter Noll.

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