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François Massieu and the thermodynamic potentials

François Massieu et les potentiels thermodynamiques

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ABSTRACT

The thermodynamic potentials have first been introduced in 1869 by François Massieu under the name of "fonctions caractéristiques" in two short articles published in the *Comptes rendus de l'Académie des sciences*. Motivated by applications to thermal engines, he showed how such a single function encompasses all properties of a fluid, linking its equation of state to its thermal properties. The conceptual interest of Massieu's functions was acknowledged many decades later.

RÉSUMÉ

Les potentiels thermodynamiques ont été inventés par François Massieu, qui les a introduits sous le nom de « fonctions caractéristiques » dans deux notes publiées en 1869 aux *Comptes rendus de l'Académie des sciences*. Il y montre comment toutes les propriétés d'un fluide peuvent se déduire d'une fonction unique, puis présente une application de la relation ainsi établie entre équation d'état et propriétés thermiques aux machines à vapeur. L'intérêt conceptuel des fonctions de Massieu n'a été reconnu que plusieurs dizaines d'années plus tard.

1. Thermodynamics till 1865

Thermodynamics as a modern science was born in 1824 with Sadi Carnot's book, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, his only scientific publication, where he introduced what would become the second law of thermodynamics. Being too much aimed at technical applications to draw the attention of scientists, and being too theoretical for engineers, this work remained nearly unknown until it was publicized and reformulated more mathematically by Émile Clapeyron [1] in 1834.

It is noteworthy that, starting from Carnot and Clapeyron, most French scientists having contributed to thermodynamics were inspired by thermal engines. Among the many scientists who elaborated the First Law throughout Europe in the 1840s, Marc Seguin [2] (as well as Rankine in Scotland) was directly involved with railways and locomotives, Gustave Hirn [3] was

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in charge with the steam engines of a family factory – whereas the other people currently credited for the establishment of the first law (Colding, Grove, Helmholtz, Joule, Liebig, Mayer) did not share this concern and had different interests. A very large number of studies about steam engines were thus published in the *Comptes rendus* between 1835 and 1855. Some of them [2,4,5] keep track of the controversy between Joule and Mayer, who both claimed priority about the idea and about the experimental determination of the mechanical equivalent of heat.

By 1865, the bases of thermodynamics had been settled through introduction of the concepts of energy, absolute temperature, and entropy. It became possible to refine the mathematical structure of the theory, and to develop tools adapted to tackle concrete problems. Among these tools, the thermodynamic potentials present a major practical importance, as all macroscopic properties of a material at equilibrium can thereby be derived from such a single function. This idea was discovered in 1869 by François Massieu, again in the prospect of improving steam engines [6].

2. Massieu (1832–1896)

A detailed biography of Massieu written by a colleague of his [7] has been published soon after his death. It includes quotations about his conceptions of science, and is followed by the speeches delivered at his funerals. We extract from it the main features of his life. François, Jacques, Dominique Massieu was born in 1832 at Vatteville-la-Rue, a small town of Normandy. Issued from a modest family, he had lost his father before his birth; a teacher helped him to pursue his studies until he was admitted in 1851 at the "École polytechnique", 39 years after Carnot. And like Carnot, he was appointed by the government at the end of his studies as an engineer while devoting his spare time to physics and mathematics. His official position, "ingénieur du Corps des mines", led him to supervise industry, railways, and mining. He worked first during a few years in Saint-Etienne and Caen, then between 1861 and 1887 in Rennes. There, he controlled the regional railway company, created a laboratory for industrial and agricultural chemistry, improved water supply, established a sewerage system. His career, as a highest ranking official, ended up in Paris, where he died in 1896. He left the memory of a both rigorous and benevolent person.

Throughout his life, he had also tackled various scientific topics. In 1861, he defended at the Sorbonne a pair of theses [8], the first one about the integration of equations of motion in analytical mechanics, the second one about the geometry of polarized waves in birefringent crystals. His doctoral degree allowed him to straightaway become Professor of mineralogy and geology at the university of Rennes, where he taught and researched in parallel with his administrative tasks. He published the local geological map. He tried to determine the age of the Earth by a study of its cooling and by using data about the underground temperature. This idea, initiated by Buffon, then made more quantitative by Fourier, had recently (in 1862) been revived by William Thomson, future lord Kelvin. Much later, Massieu turned to technology. He developed a theory of the stability and adherence of locomotives on curved or sloping railroads, and he established a method of conception for the railway interlocking systems that ensure the security of interconnected rail junctions and signals.

His main scientific achievement, the invention (in 1869) of thermodynamic potentials, also originated from his interest in railways. Both a physicist and an engineer as Sadi Carnot, Massieu had like him a dual purpose: deepening the bases of thermodynamics through a synthesis of its principles, and providing a rational theory of heat machines based on thermodynamics. Optimizing their operation requires mastering the properties of water, which were not easy to measure under the required conditions, especially for superheated steam. Theoretical information was therefore valuable.

3. The publication in the *Comptes rendus* (1869)

Massieu published two successive short articles, clearly written, in the *Comptes rendus* [6]. The first one summarizes a memoir that he presented at the "Académie des sciences" on 18 October 1869; the second one adds details. We reproduce here Massieu's reasoning, which relies on differential calculus. He first notes that, when an infinitesimal amount δQ of heat is yielded to a material, it can generate three effects, produce external work $p\mathrm{d}V$, produce "internal work", and raise the "detectable heat". Owing to the equivalence between heat and work, the latter two quantities cannot be distinguished, and only their sum $\mathrm{d}U$ occurs. This is expressed[1] by $\delta Q = \mathrm{d}U + p\mathrm{d}V$.

Next, Massieu recalls that, because of Joule's and Carnot's principles, the integral of $\delta Q/T$ over any closed reversible cycle vanishes, a property which implies that $\delta Q/T$is an exact differential,[2] namely, the differential $\mathrm{d}S = \delta Q/T$ of the entropy S introduced a few years earlier by Clausius. Replacing therein δQ by its above expression, he writes

$$\mathrm{d}S = \frac{\mathrm{d}U}{T} + \frac{p}{T}\mathrm{d}V$$

[1] Massieu specifies that he refers to 1 kg of matter. He names U "chaleur interne" and expresses it in kilocalories, the former unit of heat. (In his memoir of 1876, he mentions that, depending on the authors, U is called "internal heat" or "internal energy".) He implicitly uses as unit of force the kilogram-force, expressing pressure in kgf·m^{-2} and work in kgf·m. Hence, his formula contains in front of $p\mathrm{d}V$ a factor $A = 1/424$ which arises from 1 kcal $\sim$ 424 kgf·m and which we disregard.

[2] Massieu expresses the temperature t in Celsius degrees, and introduces also the absolute temperature $T = t + 273$. He uses the same notation "d" for a differential, for a small amount "δ", and for a partial derivative ∂, although he stresses in his memoir of 1876 that "d" in his "$\mathrm{d}Q$" should carefully be distinguished from an exact differential. We slightly change the typography of his formulae, and use SI units (joule for both heat and work, kelvin for temperature).

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