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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.

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R É S U M É

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.

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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 $p dV$, 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 dU occurs. This is expressed¹ by $\delta Q = dU + p dV$.

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 $dS = \delta Q/T$ of the entropy S introduced a few years earlier by Clausius. Replacing therein δQ by its above expression, he writes

$$dS = \frac{dU}{T} + \frac{p}{T} dV$$

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 $\text{kgf}\cdot\text{m}^{-2}$ and work in $\text{kgf}\cdot\text{m}$. Hence, his formula contains in front of $p dV$ a factor $A = 1/424$ which arises from $1 \text{ kcal} \sim 424 \text{ kgf}\cdot\text{m}$ 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 “dQ” 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).

Massieu notes that S and U are functions of the independent variables that characterize the state of the material, to wit, for a fluid, two variables chosen among T , p , and V . Selecting T and V , he expresses dS in the form $XdT + YdV$, where X and Y depend on the partial derivatives of U . Hence the equality $\partial X/\partial V = \partial Y/\partial T$ of cross derivatives yields $\partial (p/T)/\partial T = \partial (U/T^2)/\partial V$. Massieu deduces from this equality that

$$U \frac{dT}{T^2} + \frac{p}{T} dV = d\psi$$

is the exact differential of some function $\psi(T, V)$, which depends on the material and which he calls “fonction caractéristique du corps”.

He justifies thereafter this name of “first characteristic function” by showing that any thermodynamic property of the material can directly be obtained from $\psi(T, V)$ – through partial first derivatives for U , p and S , and through partial second derivatives for specific heats, expansion coefficients and compressibility. He also exhibits the relation:

$$\psi = S - \frac{U}{T}$$

Likewise, by expressing dS in terms of the independent variables T and p , he proves that

$$(U + pV) \frac{dT}{T^2} - V \frac{dp}{T} = d\psi'$$

is an exact differential. This defines a “second characteristic function” $\psi'(T, p)$, which alternatively embeds all thermodynamic properties of the material, and which is equal to

$$\psi' = S - \frac{U}{T} - \frac{pV}{T}$$

The existence of two characteristic functions introduces the idea of natural variables in terms of which a thermodynamic potential should be expressed, T, V for ψ , and T, p for ψ' .

In the continuation of his first article in the *Comptes rendus* and in the second one, Massieu specializes to water, relevant for steam machines. He successively applies the idea of characteristic functions to the gas, to the saturated steam, and to the superheated steam on which few experiments had so far been performed. He writes explicit expressions for either ψ or ψ' , constructing them in terms of the sole thermal properties. He compares some formulae issued from these expressions with experimental results. He stresses that, by relying on characteristic functions, one can, on the one hand, use theory to determine some quantities not yet measured, and, on the other hand, check the consistency with thermodynamics of experimental data, and prove or disprove the compatibility of empirical formulae. Indeed, the equation of state of a material and its thermal behavior are not independent, as both must result from the same characteristic function.

4. The memoir of 1876

Massieu published in 1876 a long memoir [9] of 92 pages, including a systematic account of the ideas he had expressed in the *Comptes rendus* and developing the work he had outlined there. He stresses that U and S are not independent functions of T and V , but are issued from a single characteristic function that also provides the equation of state $p(T, V)$. He presents detailed proofs for both general results and applications, and readily derives from the existence of a characteristic function all the general equations that relate the thermodynamic coefficients to one another. Accordingly, he advocates the description of a material by its characteristic function rather than by these traditional coefficients. In fact, such a function, once it is determined from the available data, synthesizes all properties of the material and embeds their mutual links issued from thermodynamics.

Some phenomenological results of H. Regnault or W. Thomson are thus recovered. Massieu also refutes a statement by Hirn, who claimed to have shown, for an arbitrary fluid expanding without exchange of heat nor work, that the product pV remains unchanged; he proves that this property holds only if the characteristic function satisfies some equation, and hence cannot be general.

The second half (46 pages) of this memoir is entirely devoted to applications to superheated water steam, for which the only reliable data, measured by Regnault, was the specific heat under atmospheric pressure, averaged between 120 and 220 °C. Complementing it with information about saturated steam and making some reasonable hypotheses, Massieu constructs a semi-empirical expression of the characteristic function, in the prospect of improving the operation of steam machines by use of moderate superheating.

“Following the good advice” of Joseph Bertrand, the “secrétaire perpétuel” of the “Académie des sciences” to whom the memoir was presented, Massieu had substituted to his former characteristic functions ψ and ψ' the functions $H = T\psi = TS - U$ and $H' = T\psi' = TS - U - pV$, to slightly simplify the formulae. We shall see below that this seemingly innocuous replacement was in fact conceptually unfortunate!

5. A late recognition

Massieu's pioneering contribution had little impact, maybe because his incentive looked technical (although he wrote in a scientific style and accounted for the most recent advances such as Clausius's entropy). Even presently, most textbooks still ignore him, crediting Gibbs for the invention of thermodynamic potentials. In fact, as it is well known, Gibbs [10] introduced in 1876, under the name of "fundamental function" what we now call the "free enthalpy"

$$G(T, p, \{N_i\}) = U - TS + pV$$

for a fluid made of $\{N_i\}$ molecules of different species. However, Gibbs himself had clearly written in a footnote: "Massieu appears to have been the first to solve the problem of representing all the properties of a body of invariable composition which are concerned in reversible processes by means of a single function." In fact, Gibbs's function can be regarded as an extension of Massieu's second characteristic function to a mixture that may undergo chemical reactions.

Likewise, the "free energy" $F(T, p, \{N_i\}) = U - TS$ introduced in 1882 by Helmholtz [11] appears as an extension to mixtures of Massieu's first characteristic function. Duhem [12], who proposed to term all these functions "thermodynamic potentials", properly attributes their idea to Massieu, and their introduction in thermochemistry to Gibbs. The same credits are given by Poincaré [13], who as Duhem presents Massieu's functions in their modified form H and H' of 1876. However, Planck's potential [14] is nothing but the original form ψ' of Massieu's second characteristic function; Planck, as many others, seems to have been unaware of Massieu's work.

The conceptual interest of Massieu's original thermodynamic potentials ψ and ψ' began to be emphasized only one century later, by Callen [15]. To clarify the status of Massieu's functions in modern physics, we feel useful at this point to recall Callen's general formulation of the principles of thermodynamics. The compound isolated system under study is analyzed into subsystems, each of which is at thermal equilibrium. The state of each subsystem, a homogeneous piece of material, is characterized by some extensive variables, such as U , V , N for a simple fluid (plus other quantities for ordered materials, for chemical or for electromagnetic phenomena). These variables are conservative when exchanges (of energy, of volume or of particles) may take place between subsystems, a generalization of the first law. The existence of entropy, a function S of the extensive variables, is then postulated: for each subsystem, S is a continuous, differentiable, concave, positive and extensive function; for several subsystems, it is additive. Consider a situation when some exchanges between subsystems, formerly inhibited, become allowed. At the end of the process, the set of extensive variables that characterizes the state of the considered isolated compound system are submitted to constraints issued from their initial values and imposed by the conservation laws; under these constraints, their actual values when equilibrium is reached are determined by looking for the maximum of the entropy function. This is Callen's main principle, which encompasses the various earlier forms of the second law. Finally, for each subsystem, an infinitesimal shift of equilibrium, characterized for a fluid by variations dU , dV , dN , produces a change of entropy

$$dS = \gamma_U dU + \gamma_V dV + \gamma_N dN$$

where γ_U , γ_V , γ_N are the intensive variables conjugate to U , V , N , respectively. They are interpreted, in terms of the traditional intensive variables entering $dU = TdS - pdV + \mu dN$, as

$$\gamma_U = \frac{\partial S}{\partial U} = \frac{1}{T}, \quad \gamma_V = \frac{\partial S}{\partial V} = \frac{p}{T}, \quad \gamma_N = \frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

The zeroth law, applied to pairs of subsystems that may exchange heat, and its generalizations to other conservative variables, readily result from this definition of intensive variables and from the stationarity of entropy at equilibrium.

In this modern and unifying formulation of the foundations of thermodynamics, the entropy S has a specific status, facing the conservative variables such as U , V , N that lie on the same footing. The resulting *fundamental differential form*, defined as $dS = \gamma_U dU + \gamma_V dV + \gamma_N dN$, separates the quantities having a different nature, S on the one hand, U , V , N on the other hand, in contradiction with the traditional differential form $dU = TdS - pdV + \mu dN$. Starting from the entropy function $S(U, V, N)$ instead of $U(S, V, N)$, Callen's approach is more rational from a conceptual viewpoint, and should supersede the approaches based on energy. There the function S directly appears as the *fundamental thermodynamic potential*, from which any thermodynamic property can be found through partial differentiation owing to the very definition of intensive variables.

Accordingly, performing in a standard way a change of variables by means of a *Legendre transform* of $S(U, V, N)$ produces other thermodynamic potentials. This procedure produces in a natural way Massieu's characteristic functions in their *original form* ψ and ψ' as thermodynamic potentials. His first function $\psi(\gamma_U, V, N) = S - \gamma_U U$ is nothing but the Legendre transform of $S(U, V, N)$ with respect to U , which interchanges the roles of U and γ_U . Likewise, Massieu's second function $\psi'(\gamma_U, \gamma_V, N) = S - \gamma_U U - \gamma_V V$ is the Legendre transform of $S(U, V, N)$ with respect to U and V . However, its natural variables replacing U and V are not T and p as Massieu wrote, but $\gamma_U = 1/T$ and $\gamma_V = p/T$. Indeed, Massieu's formulae that we recalled above are simplified by this replacement. We should ultimately regard ψ and ψ' as thermodynamic potentials more fundamental than the traditional potentials $F(T, V, N) = -T\psi$ and $G(T, p, N) = -T\psi'$ issued from $U(T, V, N)$, notwithstanding the practical interest of the latter.

This conclusion is enforced when thermodynamics is derived as a macroscopic consequence of quantum statistical mechanics applied to systems at equilibrium. A basic conceptual role is then devoted to the von Neumann entropy, interpreted

as missing information: looking for its maximum under constraints on the conservative variables provides the Boltzmann–Gibbs distributions [16]. The value of this maximum is readily identified with the thermodynamic entropy S , while Massieu's potentials ψ and ψ' are directly recovered as *logarithms of partition functions*. For instance, canonical equilibrium, characterized by the constraint $\langle H \rangle = U$ on the average Hamiltonian, is described by the canonical distribution $\exp(-\beta H)/Z_c$, where β is the Lagrange multiplier associated with the constraint, where Z_c is the canonical partition function and where $U = -\partial \ln Z_c / \partial \beta$. While β is identified with $1/k_B T$, where $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann's constant,³ Massieu's function $\psi(\gamma_U, V, N)$ is identified with $k_B \ln Z_c$, in agreement with the relations $\gamma_U = k_B \beta$, $U = -\partial \psi / \partial \gamma_U$, and $S = \psi + \gamma_U U$.

The fact that Massieu's original functions ψ and ψ' of 1869 should be regarded as the most natural thermodynamic potentials, either as Legendre transforms of the entropy function or as logarithms of partition functions, is slowly getting recognition. Massieu's name, which was not yet mentioned in Gillispie's dictionary [17], now appears in Wikipedia.

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³ The fundamental nature of $\beta = 1/k_B T$ rather than T is confirmed by the consideration of systems with a bounded energy spectrum, such as spin systems, which can be set in equilibrium states with negative temperatures. The adequate temperature scale is then clearly not T , but $\gamma_U = 1/T = k_B \beta$, which continuously varies from $+\infty$ to $-\infty$ when U varies from the lower to the upper bound of the spectrum.