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Constantin Carathéodory and the axiomatic thermodynamics

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The birth, raise, development and fortunes of a fundamental theory in thermodynamics, the axiomatic thermodynamics, a creation of Constantin Carathéodory, is thoroughly presented together with a summary of Carathéodory's biography. Axiomatic thermodynamics is centered around some interesting properties of Pfaffian differential equations, which are here introduced and used for some well-known cases in thermodynamics.

KEY WORDS: axiomatic thermodynamics, Constantin Carathéodory, Pfaffian differential equations

There is no branch of mathematics, however abstract, which may not some day be applied to phenomena of the real world

Lobatchewsky

1. Introduction

In 1909 Constantin Carathéodory, a skilled mathematician of the German mathematics school, published a seminal work on an axiomatic approach to thermodynamics, which practically put the entire subject on a new basis. His method allowed a rigorous mathematical formulation of the consequences of the second thermodynamic law (or postulate). In Carathéodory's treatment thermodynamics is built up as a kind of extension of mathematics. The mathematics of the axiomatic treatment is centered around the geometric behavior of a certain differential equation, known as Pfaffian, and its solutions. As a result he was able to obtain a purely formal thermodynamics without the recourse to the well-known XIXth century principle of Thomson and Clausius of the impossibility of a "perpetuum mobile" of the second kind, and without recourse to imaginary machines or imaginary cycles, and such strange concepts as the flow of heat.

The geometrical flavour of thermodynamics can clearly be noticed with the formulation of the zeroth law of thermodynamics, which practically defines temperature, but which concerns thermal equilibrium, that is, "*if* t_1, t_2 *and* t_3 *are equilibrium states of three systems such as* t_1 *is in thermal equilibrium with* t_2, *and* t_2 *is in thermal equilibrium with* t_3, *then* t_3 *is also in thermal equilibrium with* t_1". This law strongly resembles the first axiom of Euclidean geometry (ca. 300 BC), that is, "*things equal to the same thing are equal to one another*".

Before entering into the argument the fundamental difference between a mathematical formulation and a mathematical derivation should be mentioned. What has been achieved in Carathéodory's treatment is a mathematical formulation and not a mathematical derivation of the laws of thermodynamics which, as any law of physics, cannot be derived mathematically.

In the present paper we will not get into the details of Carathéodory's achievement as it has already been done in a very satisfactory way by other well renowned scientists all along this century, as we shall see. Here, we will just try (i) to briefly describe Carathéodory's biography, (ii) to review the historical development of the axiomatic treatment of thermodynamics, and (iii) to elucidate some aspects of Pfaffians, the mathematical tools of axiomatic thermodynamics, normally underscored in thermodynamics textbooks.

2. Constantin Carathéodory

2.1. Life and deeds

Constantin Carathéodory (1873–1950), see figure 1, was born in Berlin but was the son of a Turkish ambassador of Greek origin [1]. In 1875 his family is residing in Bruxelles, Belgium, where in 1895 he ends his studies at the École Militaire of Belgium. He then moves to Samos, Greece, where he plans the construction of roads. After a period in London and Egypt, he returns to Berlin in 1900 where he carries further studies in mathematics. His Ph.D., on special Euler–Lagrange equations, carried under the supervision of H. Minkowski, is concluded in Göttingen in 1904. From 1905 till 1908 he is free professor in Göttingen, then in Bonn (1909) and then in Hannover (1910). He starts then a long journey through Breslau, Göttingen, Berlin, Izmir (now in Turkey), Athens (Greece), until he finally settles down in Munich (1924). At this time he is well acquainted with many famous mathematicians, like D. Hilbert (1862–1943) and H. Schwarz (1848–1921), having contributed to the theory of functions of Weierstrass, and to variational calculus and its application to optics. He is one of the founders of the generalized metric geometry, and from 1905 on he starts deepening the general theory of functions and the algebraic basis of the concept of integral. His main mathematical works are listed in the appendix, and testify his wide mathematical knowledge and interests. Nevertheless, his notoriety mainly comes from his two studies on thermodynamics. These can probably be considered his greatest scientific achievements.

Figure 1. Constantin Carathéodory (1873–1950) (from [41]; this book provides inside the cover page a series of portraits of famous scientists who contributed to thermodynamics).

2.2. Birth and origins of axiomatic thermodynamics

On thermodynamics he published a rather long paper followed many years later by a short paper. His first fundamental paper, in which he laid the basis of axiomatic thermodynamics, was published in 1909 under the title "*Untersuchungen über die Grundlagen der Thermodynamik*" (Researches on the foundations of thermodynamics) which appeared in Math. Ann. 67 (1909) 355–386. The second more explanatory and conclusive paper, "*Über die Bestimmung der Energie und der absoluten Temperatur mit Hilfe von reversiblen Prozessen*" (On the calculation of energy and of the absolute temperature with the help of reversible processes), appeared only 16 years later in Sitzber. Preuss. Akad. Wiss. Phys. Math. K1 (1925) 39–47. In his first paper he was able to obtain in a formal way the laws of thermodynamics without recourse to imaginary engines or such concepts as the flow of heat. We could wonder how did he arrive at the idea of an axiomatic thermodynamics. A short glance at his curriculum can give us some guidelines. His engineering studies at the École Militaire included many lectures on thermodynamics. Another important moment in his life, and in the life of every contemporary mathematician, was the publication in 1899 by his later colleague and friend, D. Hilbert, of the seminal work "*Grundlagen der Geometrie*" (Foundations of Geometry) where a rigorous axiomatic foundation for geometry was laid down. This work, soon recognized as one of the most important works in mathematics of our age, had also a tremendous impact on the development of mathematical physics. Exactly ten years later, in 1909, Carathéodory came out with his first work on thermodynamics, in which, centering the attention on the geometric properties of certain equations, known as Pfaffians, he attempted to "geometrize" this field of physics. Something like was doing A. Einstein (1879–1955) during those same years, 1905–1917, with gravitation. An important role in the development of the new axiomatic method was surely played by Carathéodory's friendship with M. Born (1882–1971), as we shall see in the following lines.

2.3. The axioms

In his first seminal work Carathéodory starts, quite mathematically, with three definitions, concerning equilibrium, states, and thermodynamic coordinates. He, then, goes on, introducing a first axiom about the internal energy of a multiphase system and its variation, inclusive external work, during an adiabatic process ($U_\mathrm{f} - U_\mathrm{i} + W = 0$, where f stands for final, and i for initial). This first axiom can be read as a reformulation of the first postulate of thermodynamics. After that, he states his famous second axiom, that constitutes the real novelty of his work. This axiom reads in original language, "*In jeder beliebigen Umgebung eins vorgeschriebenen Anfangszustandes gibt es Suztände, die durh adiabatische Zustandsänderungen nicht beliebig approximiert werden können*". An English version of this axiom could be, "*In the neighborhood of any equilibrium state of a system (of any number of thermodynamic coordinates), there exists states that are inaccessible by reversible adiabatic processes*". Starting with this axiom, Carathéodory shows how to derive the Kelvin temperature and every other statement of the engineering method developed during the second part of XIXth century. This axiom can be better understood when it is read together with Kelvin's formulation of the second law, that "*no cycle can exist whose net effect is a total conversion of heat into work*". Both statements have their common basis on the everyday experience, and they are just a generalization of the observed fact of nature that work cannot be fully recovered. If, for example, the one-sidedness of entropy function is exemplified by an arrow in which 1 and 2 are two adjacent non-infinitesimally close points, —1—2→(S), then the asymmetry of S does not allow transformations from 2 to 1, but only from 1 to 2, that is, 1 is inaccessible from 2, while 2 can be accessed from 1. Carathéodory's "mathematical" formulation identifies this asymmetry with unattainable "near" equilibrium states.

It can be noticed that in the axioms and definitions of the new method there is no mention of heat, temperature or entropy whatsoever. In fact, heat is regarded as a derived rather than a fundamental quantity, that appears as soon as the adiabatic restriction is removed. This can be considered the strength and the weakness of Carathéodory's approach. The weakness, as it is usually the heat added to a system that can easily be measured, but, centering the attention on energy rather than on heat renders the method quite appealing from a physical point of view (as it is energy that is conserved and not heat). In the bulk of his work he develops, with the aid of both axioms, but specially of the second, and by the aid of the theory of Pfaffian equations, the new methodology, which will bring to the introduction of the concept of entropy and its postulate as well to the introduction of the concept of thermodynamic absolute temperature.

3. The scientific community

The axiomatic treatment of Carathéodory started rather noiseless and it was only in 1921 that M. Born wrote three important articles [2–4] about Carathéodory's axiomatic treatment. After that, the axiomatic thermodynamics caught the attention of well-known physicists of those times, and particularly of A. Landé (1888–1975) [5], M. Planck (1858–1947) [6], S. Chandrasekhar (1910–1995) [7], and W. Pauli (1900–1958) [8], among others, who recognized, and in one case even sharply criticized Carathéodory's work. The importance of the attempt to dispense with the engines and cycles which are at the root of the engineering method due, mainly, to S. Carnot (1796–1832), W. Thomson, Lord Kelvin (1824–1907) and R.J.E. Clausius (1822–1888), was soon recognized. In this respect, it should be noticed that already L.F.H. Helmholtz (1821–1894), during the previous century, had remarked that to define temperature and entropy it was not necessary to invoke neither cycles nor ideal gases [9]. The formal elegance of Carathéodory's method was so appealing that many tried either to complete or to render its mathematics more palatable to a wider scientific community. Nevertheless, these last efforts did not gain a large audience among physicists and physical chemists, who normally either were rather reticent in adopting Carathéodory's axiomatic method or considered it as an interesting curiosity. Thus, it is not all odd to notice that the axiomatic method, with some exceptions [8–12], never arrived on the main pages of widely used physics, physical chemistry or just thermodynamics textbooks. Even a fundamental book on the argument, like the *Thermodynamics* by Lewis and Randall [13], did ignore the method, but, this same book included in the appendix the Bridgman shorthand method by which formulas may be obtained for any desired partial derivative, which had been proposed in 1914, i.e., shortly after the birth of Carathéodory's thermodynamics. Even in the cited exceptions [8–12] the axiomatic method is presented more as a pure curiosity than as a general foundation for thermodynamics, with the exception of [12].

If M. Born was the first renowned scientist, soon after first world war, who with a series of three studies [2–4] centered the attention on the new method, then M. Planck in 1926 [6] was the first sharp criticizer of the new method. He, in fact, concluded that the Thomson–Clausius treatment was far more reliable. Max Planck's preferences were due to the fact that Thomson's definition was much nearer to experimental evidence, i.e., to natural processes, which at the very end are the only ground on which all natural laws are erected. It is interesting to read his own words on the argument, "*hat wohl noch niemand jemals Versuch angestellt in der Absicht, alle Nachbarzustände irgendeines bestimmten Zustandes auf adiabatischen Wege zu erreichen*, . . . , *das Prinzip gibt aber kein Merkmal an, durch welches die erreichbaren Nachbarzustände von den unerrreichbaren Nachbarzustände zu unterscheiden sind*" (nobody has up to now ever tried to reach, through adiabatic steps only, every neighborhood of any equilibrium state and to check if they are inaccessible, . . . , this axiom gives us no hint which would allow us to differentiate between the inaccessible from the accessible states). Planck himself tried to put forward a treatment between Thomson–Clausius' and Carathéodory's approaches. His treatment was also based on the properties of Pfaffians.

The second important positive reflection on this topic, after Born's, came soon after the second world war from a scientist working in a far away University, H.A. Buchdahl from the University of Tasmania, Australia, who published a series of three main studies [14–16] followed, some years later, by two other papers [17,18]. Buchdahl tried to render Carathéodory's treatment more appetizing to a wider range of physicists, and especially to English speaking physicists. He was, very probably, well acquainted with the German language. In fact, he refers continuously to the original M. Born articles and to other German mathematics books. To him can be credited the fact that, soon after, axiomatic thermodynamics caught the attention of American and English physicists. It is to be noticed that Buchdahl published not only a book on thermodynamics [19] but also a book on Hamiltonian optics [20] in which a detailed account of the Hamiltonian treatment of aberration theory in geometrical optics is presented, and where many classes of optical systems are defined in terms of the symmetry they possess. Geometry seems to concern a lot those who are interested in axiomatic thermodynamics.

After Buchdahl, authors like Pippard [21], Turner [22], Sears [23], and Landsberg [24] presented an interesting series of works, with the initial aim to further simplify the mathematics of the axiomatic method. But this school of thought soon realized that it was a rather unfruitful effort, and, thus, it ended by demonstrating the equivalence between Carathéodory's axioms and the Kelvin–Planck statement of the second postulate. Now, the two methods can be considered equivalent, and the only superiority of Carathéodory's method being that it focuses the attention on the system, its coordinates and states, which are normally overlooked in the normal engineering approach. It should not be underscored the fact that some of these authors published interesting works on thermodynamics and on physical theory [25–29] and that Landsberg published in 1956 [30] an interesting and detailed development of the axiomatic method of Carathéodory. This last work certainly played no minor role in Landsberg's deduction [24] of Carathéodory's principle from Kelvin's principle.

Looking back at the history of this elegant mathematical method, it really seems that M. Planck's criticism about the difficulty of the method to provide a compelling physical picture of entropy stands even today as the main difficulty, together with its mathematical "harshness", for a wide acceptance of Carathéodory's treatment. Quite probably these two difficulties are equivalent, as, as soon as the compelling physical picture is considered insufficient, the mathematical "harshness" becomes practicable, and as soon as the mathematical "harshness" becomes intelligible, the compelling physical picture is considered incomplete.

4. The Pfaffians

Before introducing the Pfaffians let us first spend two words about the meaning of the term axiomatic. An axiomatic system is an ensemble of declarations (statements) which are the starting elements of a mathematical project, e.g., the construction and solution of a theorem. In some cases axioms are held to be self-evident, as many axioms in Euclidean geometry, while others are assumptions put forward for the sake of the argument. Axioms are considered like mathematical propositions even if during the development of the project they are not cited. They can be either geometric, arithmetic and logical. For example, $x = x$, $(x+0) = x$, $(x \cdot 0) = 0$ are arithmetic axioms, and they can be used to state some transformation rules, and to infer new formal statements, i.e., from $x = x$ we can infer $0 = 0$. The axioms and the rules of inference jointly provide the basis for proving theorems. The word "postulate" is sometimes used as a synonym for axiom, but, strictly speaking, in mathematics and logic, axioms are general statements accepted without proofs, while postulates are axioms which deal with specific subject matter and cannot be considered general statements anymore.

The mathematical tools from which evolves the axiomatic thermodynamics of Carathéodory are the Pfaffian differential equations, first studied by J.F. Pfaff (1765–1825), who proposed the first general method of integrating partial differential equations of the first order in 1814–1815. Carathéodory's arguments are, in fact, derived from the geometric behavior of Pfaffian equations and their solution. Pfaffians are, essentially, a set of partial differential equations that have kept the name of their originator. Usually, equations of thermodynamics occur in a linear differential form that once was known as Pfaff expression or Pfaff differential form

$$\mathrm{d}f = \sum X_i \, \mathrm{d}x_i, \tag{1}$$

where i runs from 1 to n, and where X_i are functions of some or all the independent variables x_i. This equation generally cannot be considered a normal differential equation. If equation (1) is equalled to zero, i.e., $\mathrm{d}f = 0$, then we have what is called a Pfaff equation.

For the sake of clarity let us limit ourselves to $i = 2$, and let it be, $x_1 = x$, $x_2 = y$, $X_1 = X_1(x, y) = X$, and $X_2 = X_2(x, y) = Y$. In this case the Pfaff expression given by equation (1) can be rewritten into the following form:

$$\mathrm{d}f = X \, \mathrm{d}x + Y \, \mathrm{d}y. \tag{2}$$

The curvilinear integral along a path C of equation (3) is path-independent if $X = \partial f / \partial x$ and $Y = \partial f / \partial y$:

$$\int_C \mathrm{d}f = \int_C [X \, \mathrm{d}x + Y \, \mathrm{d}y]. \tag{3}$$

Then, equation (1) can be rewritten into the following well-known total differential form:

$$\mathrm{d}f = \frac{\partial f}{\partial x} \, \mathrm{d}x + \frac{\partial f}{\partial y} \, \mathrm{d}y. \tag{4}$$

In this case function f is a state function, and is path-independent, i.e.,

$$f = \int_C \mathrm{d}f = f(x_2, y_2) - f(x_1, y_1), \tag{5}$$

where $P(x_2, y_2)$ and $P(x_1, y_1)$ are the end and start points of path C, respectively.

A necessary and sufficient criterium to detect a total differential equation is given by the following Schwarz relation (notice that H.A. Schwarz, 1843–1921, was Carathéodory's professor in Berlin)

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x}, \tag{6}$$

i.e.,

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}. \tag{7}$$

This criterium tells us that the Pfaff equation, $\mathrm{d}f = 0$, is an exact differential and has the following solution:

$$f(x, y) = \int \mathrm{d}f = \int X\,\mathrm{d}x + \int Y\,\mathrm{d}y = \text{const.} \tag{8}$$

Now, let us use these mathematical considerations to check some well-known thermodynamic Pfaffians.

4.1. *Adiabatic transformation of an ideal gas*

This is the kind of transformation around which Carathéodory's method turns. In this case the first law of thermodynamics can be written as

$$\mathrm{d}U = C_v\,\mathrm{d}T = \mathrm{d}W = -p\,\mathrm{d}V, \tag{9}$$

rearranging we obtain

$$C_v\,\mathrm{d}T + p\,\mathrm{d}V = 0. \tag{10}$$

For an ideal gas ($PV = RT$) this equation can be rearranged into

$$\frac{C_v}{T}\,\mathrm{d}T + \frac{R}{V}\,\mathrm{d}V = 0. \tag{11}$$

This Pfaff equation is exact, $\partial(C_v/T)/\partial V = \partial(R/V)/\partial T = 0$. There exists, then, a function, $f = f(T, V) = \text{const}$, with the following properties: $\partial f/\partial T = C_v/T$ and $\partial f/\partial V = R/V$ and

$$f(T, V) = \int \frac{C_v}{T}\,\mathrm{d}T + \int \frac{R}{V}\,\mathrm{d}V = \text{const.} \tag{12}$$

From this relation the well-known equation for an adiabatic transformation of an ideal gas can be retrieved: $TV^{\gamma-1} = \text{const}$, with $\gamma = C_p/C_v$ and $R = C_p - C_v$.

4.2. General transformation of an ideal gas

If the system is not in an adiabatic enclosure, than relationship $\mathrm{d}U = \mathrm{d}W$ is no more valid, and the system becomes asymmetric. The asymmetry can be expressed as a difference,

$$\mathrm{d}U - \mathrm{d}W = \mathrm{d}Q, \tag{13}$$

where Q is called heat. The question here arises whether each term of this equation is a state function. For an ideal gas the Pfaffian, $\mathrm{d}U - \mathrm{d}W = \mathrm{d}Q$, becomes

$$\mathrm{d}Q = C_v\,\mathrm{d}T + \frac{RT}{V}\,\mathrm{d}V. \tag{14}$$

Now, the Schwarz relation does not hold anymore, as $\partial(C_v)/\partial V = 0 \neq \partial(RT/V)/\partial T = R/V$, thus, Q is no state function, and, in fact, $\mathrm{d}Q$ is normally written as δQ.

For $\mathrm{d}W$ the problem is similar, we can rewrite the $\mathrm{d}W$ Pfaffian into the following form:

$$\mathrm{d}W = \frac{RT}{V}\,\mathrm{d}V + 0\cdot\mathrm{d}T. \tag{15}$$

Even here the Schwarz relation does not hold anymore, as $\partial(RT/V)/\partial T = R/V \neq \partial(0)/\partial V = 0$, i.e., W is no state function and, in fact, also $\mathrm{d}W$ is generally written as δW. Concerning the expression for $\mathrm{d}U$, it can be rewritten into the following way:

$$\mathrm{d}U = C_v\,\mathrm{d}T + 0\cdot\mathrm{d}V. \tag{16}$$

Here the Schwarz relation holds, as $\partial(C_v)/\partial V = \partial(0)/\partial T = 0$, and U is a state function, the well-known internal energy.

4.3. The integrating factor

In many cases it is possible to transform a non-exact Pfaffian into an exact one by the aid of a multiplicative function $T = T(x, y)$, i.e., of an integrating factor. Thus, be the Pfaff equation,

$$X\,\mathrm{d}x + Y\,\mathrm{d}y = 0. \tag{17}$$

Multiplying this expression by $T(x, y)$, we obtain the following expression:

$$TX\,\mathrm{d}x + TY\,\mathrm{d}y = 0. \tag{18}$$

Now, the introduction of the function T allows to satisfy the following Schwarz condition:

$$\frac{\partial(TX)}{\partial y} = \frac{\partial(TY)}{\partial x}. \tag{19}$$

For example, the following non-exact Pfaff equation, $(1 - xy)\,\mathrm{d}x + (xy - x^2)\,\mathrm{d}y = 0$, can be transformed, by the aid of the multiplicative factor $T(x, y) = 1/x$, into an exact differential equation, as the reader can easily check.

Another differential expression for which the Schwartz test fails is

$$\mathrm{d}f = \frac{RT}{P}\,\mathrm{d}P - R\,\mathrm{d}T. \tag{20}$$

But by the aid of the integrating factor, $T = -1/P$, the Schwartz condition is again fulfilled, and the resulting expression becomes the total differential of $V = V(T, P) = RT/P$.

And, this is what happens for δQ. It is possible to find a $T = T(\theta)$ function, where θ is some chosen empirical temperature that renders $\delta Q/T$ a state function, i.e., a total and exact linear differential form. This function is called entropy, S, and T is the absolute temperature. In this respect let us notice that

$$\mathrm{d}S = \frac{\delta Q}{T} = \frac{\mathrm{d}U + p\mathrm{d}V}{T}. \tag{21}$$

For an ideal gas this equation rearranges into

$$\mathrm{d}S = \frac{C_v}{T}\,\mathrm{d}T + \frac{R}{V}\,\mathrm{d}V, \tag{22}$$

and this Pfaffian obeys the Schwarz relation, thus, S is a state function.

This is, in an extremely concise way, the path which can be followed by the aid of Pfaffians, and it was this Pfaffian "thread" that Carathéodory followed to introduce Q, S and T. While we have here only treated the case with $i = 2$ (see equation (1)), which is rather trivial, as in this case an integrating factor always exists, Carathéodory's main and powerful result was to solve equation (1) for every case, i.e., for $i > 2$.

5. Finale

Before closing let us notice that further evolution of the axiomatic method with specialized works continued well into the 1970s and 1980s [31–33]. With these works we have the possibility to know some interesting considerations about the geometrization of thermodynamics, and to detect an application of the axiomatic method to the third law of thermodynamics [32]. Instead, [31] proposes a treatment which makes no use of the theory of Pfaffians, while [33] tells us about Carathéodory's method applied to a "*gedanken*" experiment of a laser interaction with absorbing matter. For those, instead, who are interested in deepening the axiomatic side of thermodynamics, and, further, the axiomatic treatment of physics (a topic which interested also D. Hilbert), [34–39] are worth to peruse. In the last cited work a critique of Carathéodory's axiomatic thermodynamics, from the point of view of the foundation of an axiomatic physics, is presented. In it Carathéodory's axioms are criticized as being too experimentally based.

Let us end with an interesting citation about Pfaff [40]: "*Laplace was asked one day who was the greatest mathematician in Germany, and he replied Pfaff in Germany and Gauss in Europe*."

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Appendix. Carathéodory's main mathematical works

Vorlesungen über reelle Funktionen (Lipsia, 1918) (Lectures on Real Functions).
Conformal Representation (Cambridge, 1932).
Variationsrechnung und partielle Differentialgleichungen erster Ordunung (Lipsia, 1935) (Variation Calculation and First Order Partial Differential Equations).
Geometrische Optik (Berlin, 1937) (Geometrical Optics).
Reelle Funktionen (Lipsia, 1939) (Real Functions).
Funktionentheorie (Berlin, 1950) (Theory of Functions).
Gesammelte Mathematische Schriften (München, 1954–1957) (Collected Mathematical Writings).
Mass und Integral und Ihre Algebriesierung (Basel, 1956) (Mass and Integral and Their Algebra Formalism).

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