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Conceptual polymorphism of entropy into the history: extensions of the second law of thermodynamics towards statistical physics and chemistry during nineteenth–twentieth centuries

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Abstract

After the birth of thermodynamics' second principle—outlined in Carnot's *Réflexions sur la puissance motrice du feu* (1824)—several studies provided new arguments in the field. Mainly, they concerned the thermodynamics' first principle—including energy conceptualisation—, the analytical aspects of the heat propagation, the statistical aspects of the mechanical theory of heat. In other words, the second half of nineteenth century was marked by an intense interdisciplinary research activity between physics and chemistry: new disciplines applied to the heat developed in the form of analytical, mechanical and statistical theories. Inside all these theories, entropy—the *brand-new* function that Clausius coined in his *Mechanical theory of heat*—started to play a central epistemic role. In the present paper, we analyse some steps of the historical process of conceptualisation of such function from 1850 to 1902. Particularly, we retrace the historical–foundational path that—starting from Clausius' Second Law—lead Boltzmann and Gibbs to their distinguished formulations of statistical entropy. As usual, our research has been unrolled through the analyses of primary sources and by leaning on critical readings of the secondary literature. As for the methodological approach, text analysis of historical documents constituted our privileged *modus operandi*. This paper is the expression of a collaborative historical research program focused on the thermodynamic foundations of physics–chemistry relationship; early results have already been published by the same authors upon the concepts of reversibility—and—thermal equilibrium.

Keywords Thermodynamics · Relationship physics–chemistry · Principles · Foundations · Entropy · Energy · Information · Communication theory · Order–disorder · Boltzmann · Carnot · Clausius · Gibbs · Shannon

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A state-of-the art of the physics–chemistry in nineteenth century

In 1860, Gustav Robert Kirchhoff (1824–1887) published a remarkable paper (Kirchhoff 1860) establishing, on brand new bases, an existing relationship between radiation and heat. More specifically, Kirchhoff's conceptual scaffolding allows modelling how the power of absorption, the radiating power, the chemical properties and the temperature of a body are intertwined with the wavelength of absorbed and emitted radiations. Kirchhoff's brainchild, whereon his new principles are based, entails the notion of "ideal black body", which he defines as follows:

> The proof I am about to give of the law above stated, rests on the supposition that bodies can be imagined which, for infinitely small thicknesses, completely absorb all incident rays, and neither reflect nor transmit any. I shall call such bodies *perfectly black*, or, more briefly, *black* bodies. It is necessary in the first place to investigate the radiating power of bodies of this description. (Kirchhoff 1860, p. 2; Author's italic style)

Based on that, he states his first foundational principle:

> Let C be a black body. Let its radiating power (generally indicated by E) be called *e*. It will be shown that *e* remains the same when C is replaced by any other black body of the same temperature. (Kirchhoff 1860, p. 2)

In general, in Kirchhoff's model, the wavelengths of the radiation were individually conceived. This hypothesis appeared coherent with the whole model because both its thermodynamic properties and the radiation could be studied as a set of independent components of different wavelengths.

Some thirty years later, Wilhelm Wien (1864–1928) published the results of his research program on heat radiation, whose aim was to obtain the explicit form of the radiation law, for an ideal black body, where the thermodynamics entered into new forthcoming new science at the same level of the applied mechanics (statistical mechanics).

> When a radiaion of a simple color transforms itself into a radiation of mixed colors, the entropy increases and this increase represents a compensation for the possible work obtainable. There is a complete analogy with the entropy increase of a mixture of separate gases. Also in gases, the entropy of the mixture is equal to the sum of the entropies of the individual gases as though they were alone in the container. But an irreconcilable difference lies in the fact that the diversities of the gases allow different values of entropy even at the same temperature, while here we have to do with energy that changes the entropy value only through differences in temperature. (Wien 1894, p. 160)

A multidisciplinary approach to model the heat radiation stems also from Max Planck (1858–1947). Along with all his scientific production (from the Pentalogy to the 14th December 1900 lecture[1]), Planck progressively intertwines thermodynamics, electromagnetism and combinatory methods, this latter mainly derived from Boltzmann's kinetic theory. It is interesting to remark that in these thermodynamic approaches to radiation, it is

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[1] On December 14th, 1900 Max Planck delivered his famous lecture before the Physicalische Gesellshaft, entitled "Zur Theorie des gesetzes der Energieverteilung im Normalspectrum" (Planck 1901).

central the role played by the entropy function. In particular, Planck defines the entropy as a statistical function: it is given by the famous equation $S_N = k \log W$, referred to a system of N resonators (Planck 1901, p. 556) which in this instance microscopically models the radiation. Planck's microscopic model of radiation actually has its scientific roots within a conceptual scaffolding based on the hypothesis of an "elemental chaos" (Planck 1914, p. 137) that, as far as heat is concerned, leans on Boltzmann's kinetic theory of gas. It is to notice that this *statistical* approach—in Planck's theory—is not limited to mechanics by it concerns also electrodynamics. Planck outlines these ideas as follows:

> In mechanics this [statistical approach] is done by the hypothesis[2] that the heat motion is a "molecular chaos[3]"; in electrodynamics the same thing is accomplished by the hypothesis of "natural radiation", which states that there exist between the numerous different partial vibrations (149) of a ray no other relations than those caused by the measurable mean values (compare below, Sec. 148). If, for brevity, we denote any condition or process for which such a hypothesis holds as an "elemental chaos", the principle, that in nature any state or any process containing numerous elements not in themselves measurable is an elemental chaos, furnishes the necessary condition for a unique determination of the measurable processes in mechanics as well as in electrodynamics and also for the validity of the second principle of thermodynamics. This must also serve as a mechanical or electrodynamical explanation of the conception of entropy, which is characteristic of the second law and of the closely allied concept of temperature. (Planck 1914, p. 137–138)

The "mechanical or electrodynamical explanation of the conception of entropy", which Planck refers to, is further specified after some lines as follows:

> But what mechanical or electrodynamical quantity represents the entropy of a state? It is evident that this quantity depends in some way on the "probability" of the state. For since an elemental chaos and the absence of a record of any individual element forms an essential feature of entropy, the tendency to neutralize any existing temperature differences, which is connected with an increase of entropy, can mean nothing for the mechanical or electrodynamical observer but that uniform distribution of elements in a chaotic state is more probable than any other distribution. (Planck 1914, p. 138)

Another conceptualisation of entropy, embodied inside a truly different context, stems from Josiah Willard Gibbs' (1839–1903) geometrical theory of chemical equilibrium. In particular, in Gibbs we find an epistemological extension of Clausius' Second Law (Clausius 1867, 1872; Gibbs 1892, 1899, 1906; Pellegrino et al. 2015) to model *the equilibrium of heterogeneous systems (i.e. chemical equilibrium).* More specifically, Gibbs develops his model by combining thermodynamic arguments, emerging from Clausius theory, with the methods of analytical geometry. His basic assumption is that.

> […] the leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, temperature, energy, and entropy of a given mass of the fluid in a state of thermodynamic equilibrium. (Gibbs 1906, p. 33).

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[2] L. Boltzmann, Vorlesungen uber Gastheorie 1, p. 21, 1896. Wiener Sitzungsberichte 78, Juni, 1878, at the end. Compare also S. H. Burbury, Nature, 51, p. 78, 1894.

[3] Chaos is the translation of the german "unordnung", found in Boltzmann's papers.

Gibbs' geometrical model allows establishing that the equilibrium state of an isolated thermodynamic system, undergoing a change at constant energy, corresponds to the maximum entropy state. Vice versa, at constant entropy conditions, the equilibrium is achieved when minimum energy is attained. This principle is extended to thermodynamic systems with variable chemical composition through the definition of a new thermodynamic variable, the potential, which in modern physical chemistry correspond to the intensive quantity named *chemical potential.* The difference in value of chemical potential throughout a heterogeneous system acts as driving force igniting chemical processes (*Ibidem*). Gibbs' model constitutes the foundational element for the theory of chemical equilibrium in current physical chemistry.

Chemical equilibrium constitutes a relevant *topos* that historically underwent a multidisciplinary approach. Gibbs' model represented only one approach. Another one culminated with the *kinetic* model of Guldberg-Waage.

In 1803, Claude Louis Berthollet (1748–1826) introduced the concept of chemical equilibrium in the *Essai de statique chimique* (Berthollet 1803, I), by leaning on the notion of *chemical affinity* and considering the concurrence of direct and reversal chemical reactions (Kapoor 1970–1980, pp. 73–82). Berthollet's ideas were mathematically enhanced by two Norwegian scholars—Peter Waage (1833–1900) and Cato Maximilian Guldberg (1836–1902)—which, in 1864, provided a quantitative way of dealing with *chemical affinity* between substances, hence delivering a mathematical definition of chemical equilibrium (Waage and Guldberg 1864). To simplify, the mathematical definition of chemical equilibrium *à la* Guldberg-Waage leans onto the idea that the *affinity* between substances—by definition—measures the aptitude of two substances to react and that a reactive system is in equilibrium when the affinity between the reactants of the direct reaction is the same as the one between the reactants of the reversal reaction.

This short panoramic overview—from the heat radiation theory to chemical equilibrium theory—highlighted three different conceptualizations of entropy.

1. 1894. In Wien's model, entropy mainly corresponds to a macroscopic quantity characterizing the radiation, this latter being modelled as a thermodynamic system made of a set of wavelengths.
2. 1875. Instead in Gibbs' works we assist to a process of geometrization of entropy such that entropy becomes a *steering variable*, whose geometrical behaviour serves to define the spontaneous direction of any thermodynamic transformation.
3. 1902. Finally, in Planck's theory entropy corresponds to a statistical function, which plays a pivotal role in the microscopic modelling of the radiation itself.

We have also seen that complex processes—as for example reacting chemical systems and the interaction of thermal radiation with matter—require a multidisciplinary approach to be modelled.

The structure of this paper

The exploitation of heat to obtain mechanical work represents the conceptual frame of Nicolas Léonard Sadi Carnot's (1796–1832) research[4] as well as most of all its hermeneutical readings by the 19th-century scientific community, from Rudolf Julius Emanuel Clausius (1822–1888) to William Thomson (1824–1907)[5] from William John Macquorn Rankine (1820–1872) to James Clerk Maxwell (1831–1879).[6] Nevertheless, from 1860s we also register thermodynamic arguments applied to other disciplinary domains: e.g., the theory of heat radiation[7] and the thermodynamic[8] model of chemical equilibrium.[9] In particular, the term entropy—seminally coined by Clausius inside his *new* Mechanical Theory of Heat (Clausius 1865)—underwent a process of semantic transformation and is currently found in several other scientific contexts[10] that appear clearly distinct from the aforementioned thermodynamic roots. In particular, from the end of the 19th-century, entropy started playing a central role within the new-born statistical mechanics.[11] In this paper we outline three major conceptual steps of the history of the entropy, starting from its thermodynamic definition as formulated by Clausius up to its former uses in the statistical mechanics.

Our research paper aims to analyse the foundations of statistical mechanics through two different approaches, respectively authored by Ludwig Edward Boltzmann (1844–1904) and Josiah Willard Gibbs (1839–1903). In this paper, we will analyse how both authors made use of Clausius' Second Laws to obtain two different statistical models and, accordingly, two different definitions of statistical entropy. First, we will track back the conceptual roots of the famous Boltzmann-Planck equation (Planck 1901, p. 556; Planck 1914, pp. 140–141).

$$S = k \log W + const.$$

Then, we will analyse Gibbs' reasoning that, firstly, lead him to encapsulate Clausius' Law into a geometrical model of thermodynamic equilibrium (cfr. Callen 1985). And secondly, allowed him to obtain a statistical formulation of thermodynamics and to maintain

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[4] Cfr. Carnot S. Carnot (1824, 1897, 1978, 1986), Gillipsie and Pisano (2014), Pellegrino 2019, Pisano 2010. Recently on Lazare Carnot's *Essay on Machines in General* see: Pisano, Coppersmith and Peake 2021. The other two pre-print volumes are: *Principes fondamentaux de l'équilibre et du mouvement (1803)* and *Géométrie de position (1803),* both by Pisano.

[5] Cfr Mayer (1842a, b), Clausius (1854, 1865, 1867, 1872), Thomson W. (1848–1849, 1851a, b, 1852, 1882–1911).

[6] Cfr. Pellegrino (2019), Pellegrino et al. 2015, Pisano, Anakkar, Pellegrino, Nagels (2019).

[7] For the history of the conceptualization of heat and thermal equilibrium the reader can refer to Black (1807), Chang (2004, 2012), Hess (1842), Pisano, Anakkar, Pellegrino, Nagels (2019), Laplace (1822), Lavoisier and Laplace (1784), Lavoisier (1789) [1937], 1862–1893; See also: Lavoisier and Laplace (1784), Leicester (1951), Planck (1901, 1903, 1914, 1917), Kirchhoff (1860), Wien (1894).

[8] Thermodynamic model is just one approach to chemical equilibrium (Hartely 1971; Hertz 2004). It is worth mentioning the « kinetic » approach that has its scientific root in Berthollet (1803; Kapoor 1970–1980) and Waage and Gulberg (1864, 1867).

[9] Cfr. Gibbs (1892,1902,1906, 1990), Pellegrino et al. (2016).

[10] There is a truly vast literature on the notion of entropy (and related statistical mechanics studies) in its several declinations. We report just a short selection: Buchdahl (1966), Čápek and Sheehan (2005), Kragh and Weininger (1996), Marcella (1992), Müller (2007), Nelson (1994), Pellegrino et al. (2014), Pisano (2004), Prigogine (1996, 1997), Prigogine and Kondepudi (1999), Prigogine and Stengers (1984, 1992), Strehlow (2005), Scerri (2001, 2013), Frigg (2008), Anakkar (2014).

[11] Cfr. Balian (1982), Cerciniani (1998), Jaynes (1965),Frigg (2008).

an analogical relation with Clausius' Second Law, in the specific case of reversibility. Hence, in the paper we will:

1. Shortly recall some foundational elements of Clausius' *Mechanical theory of heat*. More precisely, we will pinpoint how Clausius differently approached cyclic and not-cyclic processes. In this framework, the seminal mathematical expressions of the Second Law and the use of *archaic* thermodynamic functions—such as *inner Wärme* (H) and *Disgregation* (Z)—are briefly commented (Clausius 1867).
2. Sketch out Carathéodory's axiomatic approach (Carathéodory 1909).
3. Outline Boltzmann's mechanical model by leaning on the historical-epistemological analysis of his seminal work *Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie* (Boltzmann 1866). In this paper Boltzmann obtained—in the case of gases—the mathematical expressions of Heat (δQ) and Temperature (T), in terms of the kinetic energy of the constituent atoms (or molecules).
4. Discuss the physical meaning of Boltzmann's H-theorem (Boltzmann 1972) by leaning on the mechanical expression of Clausius' Second Law for cyclic processes that Boltzmann wrote in his 1866 paper.
5. Make explicit the reasoning that allowed Planck to deliver the famous equation that connects entropy and probability, i.e.: $S = klogW + const.$, currently known as Boltzmann's equation (Planck 1901, p. 556; Planck 1914, pp. 140–141).
6. Sketch out the foundations of Gibbs thermodynamic theory and the conceptual path through which he delivered a geometrical formulation of Clausius' Second Law (Gibbs 1906).
7. Outline Gibbs' statistical mechanics with particular focus on the statistical expression of the entropy in the case of a canonical system (Gibbs1902).
8. Discuss the formal analogy between Gibbs' statistical entropy and Shannon's function,[12] provided for the Mathematical Theory of Communication (Shannon 1948).

These epistemological speculations and consequent discussions are the results of collaborative research program in the History and Epistemology of Science (Chemistry–Physics and Physics–Mathematics Relationships). The former important results of this research program concerned the historical-epistemic reflections on the foundations of thermodynamics, including modern physics–chemistry (Pisano, Anakkar, Pellegrino, Nagels 2019). A further step of this research program will concern the conceptualization of chemical equilibrium, which will be matter of a next paper.

Clausius' Second Law and entropy

The definition of entropy[13] results from a long cognitive process that allowed Clausius to settle the complex issue of the Second Law of his *Mechanical theory of heat* in the case of not-cyclic thermodynamic transformations. Historically we can distinguish two conceptual steps. Firstly, Clausius delivered mathematical expressions of the Second Law for cyclic

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[12] Cfr. Sands and Dunning-Davies (2013).

[13] Cfr.: Carnot S. (1824), Clapeyron (1834), Fox (1969, 1971), De Donder (1920, 1928, 1931, 1934, 1936), Pisano, Anakkar, Pellegrino, Nagels (2019), Pellegrino et al. (2014), Pellegrino et al. (2016), Pellegrino et al. (2015), Cochran and Heron (2006), Pisano and Capecchi (2013, 2015, 2009).

thermodynamic processes (Clausius 1854). Then, some ten years later solved the problem of not-cyclic processes, by leaning on the introduction of specific thermodynamic functions whose semantics can be found inside the meanders of his microscopic model of matter. This subject was detailed in our previous paper (Pisano, Anakkar, Pellegrino, Nagels 2019). Anyway, it can be useful to recall the main points of this matter for better framing the next sections (Fig. 1).

Clausius' Second Law of the *Mechanical theory of heat* in the case of cyclic processes was firstly formulated in 1854. In Clausius' words we read:

> In a treatise published in 1854[14] I defined, for a given cyclic process, the quantity N that I named *uncompensated transformation* and it is defined by the equality[15]:
>
> $$N = \int \frac{dQ}{T}$$
>
> where dQ is the heat element that is exchanged between the transforming system and the heat reservoir; T consequently represents the absolute Temperature. About this quantity [*i.e.*, N], I have demonstrated that it can only be positive, or at least null at the boundary condition represented by a reversible cyclic process. (Clausius 1872, p. 144; author's translation).

In 1862, he completed his analysis and delivered the well-known inequality, representing the definitive mathematical expression of the Second Law for cyclic processes. In Clausius' words we read:

> In a later treatise[16] I have further completed the analysis. The previous expression for the uncompensated transformation concerning only cyclic processes—leaving out the symbol N—can also be written as follows:[17]
>
> $$\int \frac{dQ}{T} \leq 0$$
>
> that holds only for a cyclic process. (Clausius 1872, p. 145; author's translation).

In the same year, 1862, he proposed the following inequality, which mathematically represents the Second Law in the case of not-cyclic processes (Clausius 1867, 1872):

$$\frac{\delta Q + dH}{T} + dZ \geq 0 \tag{1}$$

In this expression we recognise two archaic quantities (no more in use today): the hidden heat (H) and the disgregation (Z) (Clausius 1872, p. 146; Pellegrino, Cerruti et al. 2015). Their physical meaning can be retraced by leaning on Clausius' microscopic model of matter. For these historical aspects of Clausius' Second Law, the reader can refer to (Pellegrino et al. 2015; Pisano, Anakkar, Pellegrino, Nagels 2019). It is worth noticing that Clausius employs the script dQ instead of the current notation δQ, to indicate partial differential.

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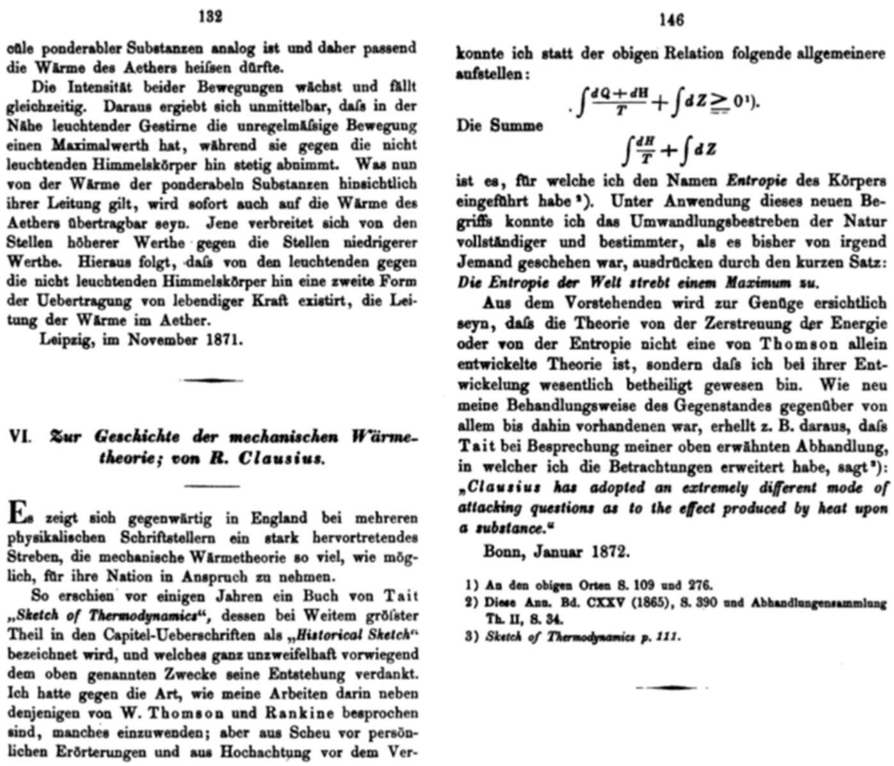
[14] Cfr. Clausius (1854).

[15] In current notation this integral should be written as:$\oint \frac{\delta Q}{T}$.

[16] Cfr. Clausius (1872).

[17] In current notation this integral should be written as: $\oint \frac{\delta Q}{T}$



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cüle ponderabler Substanzen analog ist und daher passend die Wärme des Aethers heiſsen dürfte.

Die Intensität beider Bewegungen wächst und fällt gleichzeitig. Daraus ergiebt sich unmittelbar, daſs in der Nähe leuchtender Gestirne die unregelmäſsige Bewegung einen Maximalwerth hat, während sie gegen die nicht leuchtenden Himmelskörper hin stetig abnimmt. Was nun von der Wärme der ponderabeln Substanzen hinsichtlich ihrer Leitung gilt, wird sofort auch auf die Wärme des Aethers übertragbar seyn. Jene verbreitet sich von den Stellen höherer Werthe gegen die Stellen niedrigerer Werthe. Hieraus folgt, daſs von den leuchtenden gegen die nicht leuchtenden Himmelskörper hin eine zweite Form der Uebertragung von lebendiger Kraft existirt, die Leitung der Wärme im Aether.

Leipzig, im November 1871.

VI. *Zur Geschichte der mechanischen Wärmetheorie; von R. Clausius.*

Es zeigt sich gegenwärtig in England bei mehreren physikalischen Schriftstellern ein stark hervortretendes Streben, die mechanische Wärmetheorie so viel, wie möglich, für ihre Nation in Anspruch zu nehmen.

So erschien vor einigen Jahren ein Buch von Tait „*Sketch of Thermodynamics*", dessen bei Weitem gröſster Theil in den Capitel-Ueberschriften als „*Historical Sketch*" bezeichnet wird, und welches ganz unzweifelhaft vorwiegend dem oben genannten Zwecke seine Entstehung verdankt. Ich hatte gegen die Art, wie meine Arbeiten darin neben denjenigen von W. Thomson und Rankine besprochen sind, manches einzuwenden; aber aus Scheu vor persönlichen Erörterungen und aus Hochachtung vor dem Ver-

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konnte ich statt der obigen Relation folgende allgemeinere aufstellen:

$$\int\frac{dQ+dH}{T}+\int dZ \geqq 0\,^{1)}.$$

Die Summe

$$\int\frac{dH}{T}+\int dZ$$

ist es, für welche ich den Namen *Entropie* des Körpers eingeführt habe [2]). Unter Anwendung dieses neuen Begriffs konnte ich das Umwandlungsbestreben der Natur vollständiger und bestimmter, als es bisher von irgend Jemand geschehen war, ausdrücken durch den kurzen Satz: *Die Entropie der Welt strebt einem Maximum zu.*

Aus dem Vorstehenden wird zur Genüge ersichtlich seyn, daſs die Theorie von der Zerstreuung der Energie oder von der Entropie nicht eine von Thomson allein entwickelte Theorie ist, sondern daſs ich bei ihrer Entwickelung wesentlich betheiligt gewesen bin. Wie neu meine Behandlungsweise des Gegenstandes gegenüber von allem bis dahin vorhandenen war, erhellt z. B. daraus, daſs Tait bei Besprechung meiner oben erwähnten Abhandlung, in welcher ich die Betrachtungen erweitert habe, sagt [3]): „*Clausius has adopted an extremely different mode of attacking questions as to the effect produced by heat upon a substance.*"

Bonn, Januar 1872.

1) An den obigen Orten S. 109 und 276.
2) Diese Ann. Bd. CXXV (1865), S. 390 und Abhandlungensammlung Th. II, S. 34.
3) *Sketch of Thermodynamics p. 111.*

Fig. 1 Clausius' Second Law and entropy (Clausius 1872, p. 132–146). Source: Internet Archive (public domaine). https://archive.org/stream/annalenderphysi94unkngoog#page/n161/mode/2up

In 1865, Clausius finally introduced the entropy as follows (Clausius 1865 pp. 390–391; Clausius 1872 p. 146):

$$\frac{dH}{T}+dZ \tag{2}$$

It is by leaning on this definition that the Second Law (given by Eq. 1) could be mathematically re-written as the famous inequality (Pellegrino et al. 2015; Pisano, Anakkar, Pellegrino, Nagels 2019):

$$dS \geq \frac{\delta Q}{T} \tag{3}$$

For reversible cases, it is:

$$dS = \frac{\delta Q}{T} \tag{4}$$

By integrating this latter—between initial and final states of a thermodynamic transformation—we can obtain the well-known formula:

$$S = S_0 + \int_i^f \frac{\delta Q}{T} \tag{5}$$

being S_0 the value of the entropy in the initial state. No way to determine this value (i.e. S_0) is provided in Clausius' memoirs (Clausius 1867); hence Eq. (5), whilst constituting a fundamental step forward in modern thermodynamics, cannot be exploited for entropy calculation. The issue was settled only at the beginning of the twentieth century as consequence of the *theorem of heat* formerly presented by Walther Hermann Nernst (1864–1941) in August 1905 at the University of Berlin (Nernst 1907, 1921, 1926). By analysing experimental calorimetric findings, referred to pure chemical substances in the solid state at low temperature, Nernst attained the conclusion that, when approaching absolute zero, $\Delta H(T)$ and $\Delta G(T)$ functions converge towards a same constant value (Nernst 1907; Strehlow 2005), hence—in these limit conditions—their derivatives with respect to T tend to zero.

Hence, mathematically we can write:

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_p = 0 \tag{6}$$

and

$$\lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_p = 0 \tag{7}$$

From the basic thermodynamics, we know that:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{8}$$

hence—from Eq. (6)—mathematically follows that:

$$\lim_{T\to 0}\Delta S = 0 \tag{9}$$

By physically interpreting these results, Max Planck (Planck 1917, 1991; Ebeling 2008) reformulates Nernst discoveries stating that, when approaching absolute zero, entropy asymptotically approaches a definite value that is independent from the system state variables:

> This gap in the theory has been filled by a theorem, which was developed by W. Nernst in 1906, and which, since then, has been amply verified by experience. The gist of the theorem is contained in the statement that, as the temperature diminishes indefinitely the entropy of a chemical homogeneous […] body of finite density approaches indefinitely near to a definite value, which is independent of the pressure, the state of aggregation and of the special chemical modification. (Planck 1917, p. 273)

In other words, when approaching absolute zero, the entropy results independent from any state variables; hence, its value can be arbitrarily defined without affecting the representation of the thermodynamic state of the given system. This phenomenological behaviour, up a certain limit, allows solving the problem of determining the absolute value of entropy,[18]

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[18] Cfr. Thomsen and Bers (1996), Tolmann and Fine (1948), Tishin and Spichkin (2016).

S_0, in Clausius' formula (Eq. 5), assuming that S_0 zeroes at $T = 0$ K. In Planck's words this read as follows[19]:

> It is easy to see that since the value of the entropy contains an arbitrary additive constant, that, without loss of generality, we may write $\lim\limits_{T\to 0} \mathit{entropy} = 0$. *The Nernst heat theorem then states that, as the temperature diminishes indefinitely, the entropy of a chemical homogeneous body of finite density approaches indefinitely near to the value zero.* The additive constant a of all chemical homogeneous substances in all states has herewith been uniquely disposed of. We can now in this sense speak of an absolute value of the entropy. (Planck 1917, p. 274).

Further comments on Nernst theorem and the third principle of thermodynamics stand outside the scope of this research.

Carathéodory's axiomatical approach to thermodynamics

Constantin Carathéodory (1873–1950) developed a theoretical approach to thermodynamics by leaning on a method that allows building up "[…] thermodynamics as a kind of extension of mathematics […]" (Pogliani and Berberan-Santos 2000), hence delivering one of the first axiomatic approach to a physical theory. In other words, Carathéodory obtained a purely abstract formal system without any reference to phenomenological principles in contrast with the approach of Clausius. Clausius' First and Second Law explicitly lean on the *principle of equivalence* and on the *phenomenological approach* (derived from S. Carnot; see Pisano's works; Gillispie and Pisano 2014) stating that *heat cannot flow by itself from a system at lower temperature towards one at higher temperature*. Conversely, Carathéodory's model is grounded on the theory of differential equations and on the concept of adiabatic accessibility. In particular, the concept of adiabatic accessibility allowed him to approach the second Law of Thermodynamics through the following axiom:

> In any neighbourhood of an arbitrarily given initial state there are states which cannot be reached through adiabatic transformations. (Carathéodory 1909, p. 363). Author's translation.

Adiabatic transformations do not involve heat exchange that is to say that they take place as purely mechanical phenomena. Hence, Carathéodory's formulation of the Second Law also implies that Thermodynamics is irreducible to Mechanics. In fact, in the neighbourhood of any initial thermodynamic state there are states that cannot be mechanically reached from the initial one (Fig. 2).

Within Carathéodory's formal system, the definition of entropy stems from the syntactic structure of the model, which is grounded on the behavior of a set of differential equations, known as Pfaffian.[20] Just to fix the ideas, a Pfaff's expression is given by the following differential form:

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[19] Cfr. Nernst (1926, pp. 75–90), Nernst (1907, pp. 41–50), Strehlow (2005).

[20] The adjective Pfaffian comes from Johann Friedrich Pfaff (1765–1825) who, in 1814–1815, developed a general technique for integrating partial differential equations of the first order (Pogliani and Berberan-Santos 2000).

$$df = \sum_i X_i dx_i \tag{10}$$

where the index i runs from 1 to n and X_i are functions of the independent variables x_i. If Eq. (10) zeros, i.e. $df = 0$, then we have what is called a Pfaff equation or Pfaffian. For example, let us consider the case wherein $i = 2$ and $x_1 = x$, $x_2 = y$, $X_1 = X_1(x, y) = X$, and $X_2 = X_2(x, y) = Y$. Hence, the Pfaff expression given by Eq. (10) becomes:

$$df = Xdx + Ydy \tag{11}$$

and the corresponding Pfaffian is:

$$Xdx + Ydy = 0 \tag{12}$$

A Pfaffian is an exact differential or path-independent differential equation if its curvilinear integral along an arbitrary assigned path C, as given by the following expression:

$$\int_C df = \int_C \left[Xdx + Ydy\right] \tag{13}$$

does not depend on C. Thus its general solution is:

$$f = \int_C df = f\left(x_2, y_2\right) - f\left(x_1, y_1\right) \tag{14}$$

where $\left(x_1, y_1\right)$ and $\left(x_2, y_2\right)$ correspond to the coordinates of points of path C, defining the integration limits. In this case, the function f corresponds to a state function. The necessary and sufficient condition for a differential to be path–independent are expressed by the following Schwarz[21] relation:

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} \tag{15}$$

Let us consider an application of Carathéodory's formal system to the thermodynamic transformation of an ideal gas (Pogliani and Berberan-Santos 2000). The differential expression of the First Law for such a system can be written as the Pfaffian:

$$dU - dW = dQ \tag{16}$$

which for one mole of an ideal gas becomes:

$$dQ = C_v dT + \frac{RT}{V} dV \tag{17}$$

Since we have $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$ and $\left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V = \frac{R}{V}$, it results that:

$$\left(\frac{\partial C_v}{\partial V}\right)_T \neq \left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V \tag{18}$$

that is to say that the Schwarz conditions are not satisfied and dQ is not an exact (or path-indipendent) Pfaffian and it has to be written as δQ.

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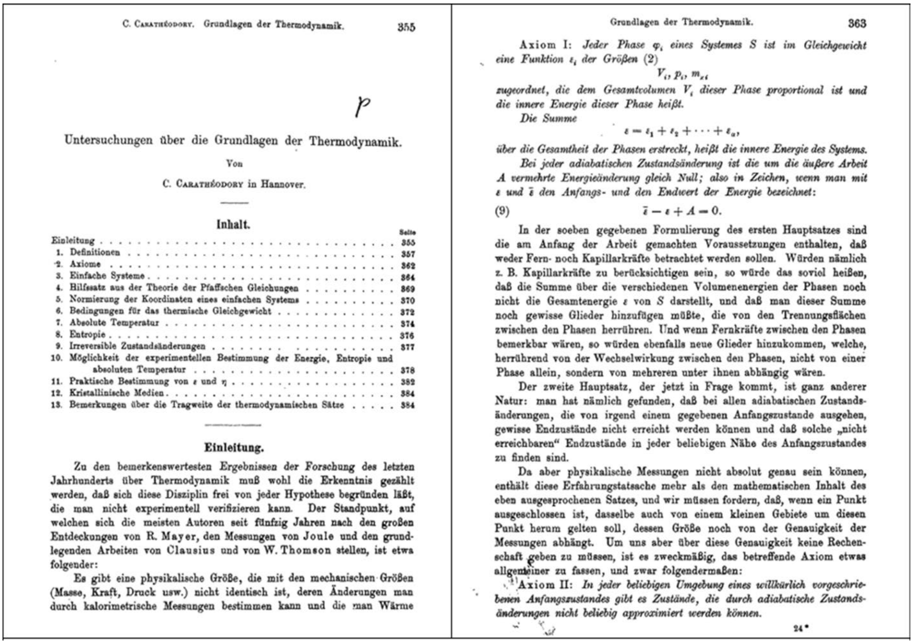
[21] Karl Hermann Amandus Schwarz (1843–1921) was Carathéodory's professor in Berlin.



C. Carathéodory. Grundlagen der Thermodynamik. 355

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Untersuchungen über die Grundlagen der Thermodynamik.

Von

C. Carathéodory in Hannover.

Inhalt.

Einleitung.

Zu den bemerkenswertesten Ergebnissen der Forschung des letzten Jahrhunderts über Thermodynamik muß wohl die Erkenntnis gezählt werden, daß sich diese Disziplin frei von jeder Hypothese begründen läßt, die man nicht experimentell verifizieren kann. Der Standpunkt, auf welchen sich die meisten Autoren seit fünfzig Jahren nach den großen Entdeckungen von R. Mayer, den Messungen von Joule und den grundlegenden Arbeiten von Clausius und von W. Thomson stellen, ist etwa folgender:

Es gibt eine physikalische Größe, die mit den mechanischen Größen (Masse, Kraft, Druck usw.) nicht identisch ist, deren Änderungen man durch kalorimetrische Messungen bestimmen kann und die man Wärme

Grundlagen der Thermodynamik. 363

Axiom I: *Jeder Phase φ_i eines Systemes S ist im Gleichgewicht eine Funktion ε_i der Größen* (2)

$$V_i, p_i, m_{\varkappa i}$$

zugeordnet, die dem Gesamtvolumen V_i dieser Phase proportional ist und die innere Energie dieser Phase heißt.

Die Summe

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_\alpha,$$

über die Gesamtheit der Phasen erstreckt, heißt die innere Energie des Systems.

Bei jeder adiabatischen Zustandsänderung ist die um die äußere Arbeit A vermehrte Energieänderung gleich Null; also in Zeichen, wenn man mit ε und $\bar{\varepsilon}$ den Anfangs- und den Endwert der Energie bezeichnet:

$$\bar{\varepsilon} - \varepsilon + A = 0. \tag{9}$$

In der soeben gegebenen Formulierung des ersten Hauptsatzes sind die am Anfang der Arbeit gemachten Voraussetzungen enthalten, daß weder Fern- noch Kapillarkräfte betrachtet werden sollen. Würden nämlich z. B. Kapillarkräfte zu berücksichtigen sein, so würde das soviel heißen, daß die Summe über die verschiedenen Volumenenergien der Phasen noch nicht die Gesamtenergie ε von S darstellt, und daß man dieser Summe noch gewisse Glieder hinzufügen müßte, die von den Trennungsflächen zwischen den Phasen herrühren. Und wenn Fernkräfte zwischen den Phasen bemerkbar wären, so würden ebenfalls neue Glieder hinzukommen, welche, herrührend von der Wechselwirkung zwischen den Phasen, nicht von einer Phase allein, sondern von mehreren unter ihnen abhängig wären.

Der zweite Hauptsatz, der jetzt in Frage kommt, ist ganz anderer Natur: man hat nämlich gefunden, daß bei allen adiabatischen Zustandsänderungen, die von irgend einem gegebenen Anfangszustande ausgehen, gewisse Endzustände nicht erreicht werden können und daß solche „nicht erreichbaren" Endzustände in jeder beliebigen Nähe des Anfangszustandes zu finden sind.

Da aber physikalische Messungen nicht absolut genau sein können, enthält diese Erfahrungstatsache mehr als den mathematischen Inhalt des eben ausgesprochenen Satzes, und wir müssen fordern, daß, wenn ein Punkt ausgeschlossen ist, dasselbe auch von einem kleinen Gebiete um diesen Punkt herum gelten soll, dessen Größe noch von der Genauigkeit der Messungen abhängt. Um uns aber über diese Genauigkeit keine Rechenschaft geben zu müssen, ist es zweckmäßig, das betreffende Axiom etwas allgemeiner zu fassen, und zwar folgendermaßen:

Axiom II: *In jeder beliebigen Umgebung eines willkürlich vorgeschriebenen Anfangszustandes gibt es Zustände, die durch adiabatische Zustandsänderungen nicht beliebig approximiert werden können.*

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Fig. 2 Carathéodory's axioms (Carathéodory 1909, pp. 355–363) Source: Internet Archive (public domain). http://www.digizeitschriften.de/download/PPN235181684_0067/PPN235181684_0067_log33.pdf

According to differential calculus, in the case of a path-dependent Pfaffian (such as δQ) it is always possible to find out an integrating factor transforming the non-exact Pfaffian into an exact one. The integrating factor of

$$\delta Q \text{ is } \frac{1}{T};$$

being T a function of the empirical temperature. In fact, by multiplying Eq. (17) by this integrating factor, it results:

$$\frac{\delta Q}{T} = \frac{C_v}{T} dT + \frac{R}{V} dV \tag{19}$$

In this case, we have $\left[\frac{\partial}{\partial V}\left(\frac{C_v}{T}\right)\right]_T = 0$ and $\left[\frac{\partial}{\partial T}\left(\frac{R}{V}\right)\right]_V = 0$ hence it follows:

$$\left[\frac{\partial}{\partial V}\left(\frac{C_v}{T}\right)\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{R}{V}\right)\right]_V \tag{20}$$

that is to say that the Schwarz conditions are satisfied hence the ratio

$$dS = \frac{\delta Q}{T}$$

is an exact Pfaffian and its integral is a state function. This was, in synthesis, the formal way that Carathéodory followed to define the entropy.

The entropy in statistical mechanics

In the history of scientific thought, the end of the nineteenth century was a period of change (Kuhn 1962; Asimov 1966), wherein experimental evidences and theoretical speculations started to challenge the dominant paradigms, hence implying a crisis of foundations inside different disciplinary communities (Truesdell 1980; Tachray 1970; Rosenfeld 1941, 1999; Prigogine 1955, 1967). This crisis culminated at the beginning of the new century and converged into a radical process of transformation concerning theories and cognitive methodologies that determined the transition from modern science—framed by Galilei and Newton[22]—to contemporary science.

It is within this period of transformations that we can contextualize the development of Statistical Mechanics,[23] whose foundations can be retraced in the seminal works on the kinetic theory of gases, authored by Clausius (1867) and Boltzmann (Boltzmann 1866, 1872, 1877). These theoretical advancements can be framed within the search for a proof of the Second Law of Clausius' *Mechanical theory of heat*. Boltzmann makes explicit this subtext in the introduction of his 1866 paper (Fig. 3):

> It is since long time that it has been widely acknowledged the coincidence of the First fundamental Law of the Mechanical Theory of Heat with the mechanical principle of kinetic energy. Conversely, the Second Law represents an exceptional peculiarity: its proof is sometimes unsure and definitely unclear. This paper's aim is to provide a truly analytic and general proof of the Second Law of the Theory of Heat, through a mechanical approach. (Boltzmann 1866, p. 9; authors' translation)

Statistical Mechanics, in general, and statistical entropy, in particular, emerged inside this groundwork and from Boltzmann's former works on they evolved towards a plurality of models and concepts. Frigg (Frigg 2008) brilliantly outlines the current status of Statistical Mechanics by writing:

> Unlike quantum mechanics and relativity theory, Statistical Mechanics has not yet found a generally accepted theoretical framework, let alone a canonical formulation. What we find in Statistical Mechanics is a plethora of different approaches and schools, each with its own program and mathematical apparatus, none of which has a legitimate claim to be more fundamental than its competitors. (Frigg, 2008 p. 6)

To handle this conceptual polymorphism, Frigg identifies two *theoretical frameworks*: the one referring to Boltzmann's approach and the one referring to Gibbs' approach. In Frigg's own words:

> In what follows I take my lead from the fact that all these different schools (or at any rate those that I discuss) use (slight variants) of either if two theoretical frameworks, one of which can be associated with Boltzmann (1877) and the other with Gibbs (1902), and can thereby classify different approaches as either 'Boltzmannian' or 'Gibbsian'. (Frigg 2008, p. 7).

On the subject, we aim to drill inside this theoretical groundwork to disclose the scientific roots of both Boltzmannian and Gibbsian models through the epistemological analysis of

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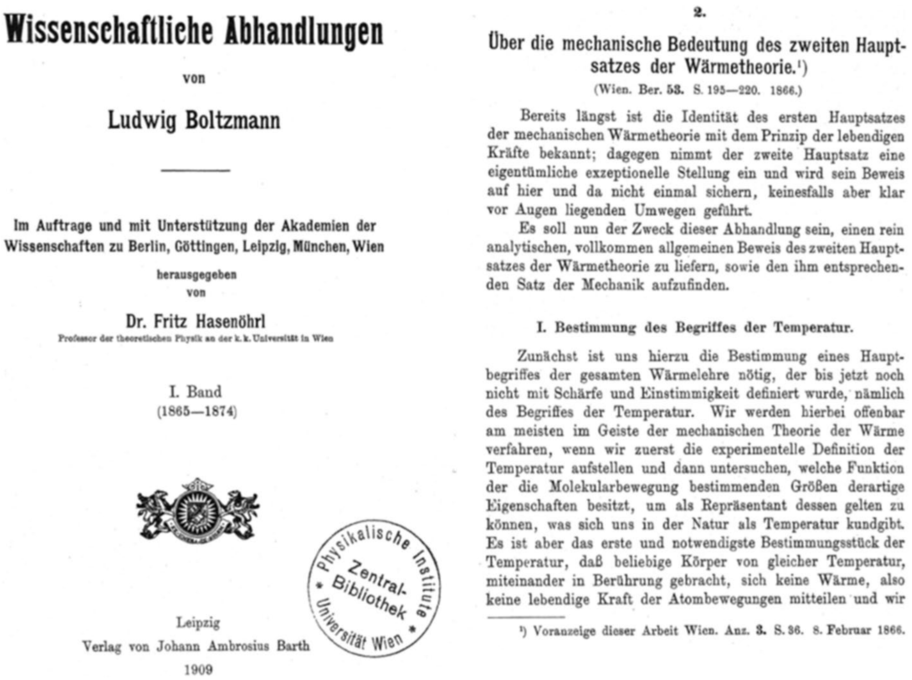
[22] Pisano and Bussotti (2020a,b, 2017a, b, 2015, 2016, 2012, 2013, 2014a, b, c), Pisano (2020), Bussotti and Pisano (2020, 2014, 2017), Pisano and Sozzo (2020).

[23] Landau and Lifchitz (1984), Nash (1957).



Wissenschaftliche Abhandlungen

von

Ludwig Boltzmann

Im Auftrage und mit Unterstützung der Akademien der
Wissenschaften zu Berlin, Göttingen, Leipzig, München, Wien

herausgegeben
von

Dr. Fritz Hasenöhrl
Professor der theoretischen Physik an der k. k. Universität in Wien

I. Band
(1865—1874)

Leipzig
Verlag von Johann Ambrosius Barth
1909

2.

Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie.[1])

(Wien. Ber. 53. S. 195—220. 1866.)

Bereits längst ist die Identität des ersten Hauptsatzes der mechanischen Wärmetheorie mit dem Prinzip der lebendigen Kräfte bekannt; dagegen nimmt der zweite Hauptsatz eine eigentümliche exzeptionelle Stellung ein und wird sein Beweis auf hier und da nicht einmal sichern, keinesfalls aber klar vor Augen liegenden Umwegen geführt.

Es soll nun der Zweck dieser Abhandlung sein, einen rein analytischen, vollkommen allgemeinen Beweis des zweiten Hauptsatzes der Wärmetheorie zu liefern, sowie den ihm entsprechenden Satz der Mechanik aufzufinden.

I. Bestimmung des Begriffes der Temperatur.

Zunächst ist uns hierzu die Bestimmung eines Hauptbegriffes der gesamten Wärmelehre nötig, der bis jetzt noch nicht mit Schärfe und Einstimmigkeit definiert wurde, nämlich des Begriffes der Temperatur. Wir werden hierbei offenbar am meisten im Geiste der mechanischen Theorie der Wärme verfahren, wenn wir zuerst die experimentelle Definition der Temperatur aufstellen und dann untersuchen, welche Funktion der die Molekularbewegung bestimmenden Größen derartige Eigenschaften besitzt, um als Repräsentant dessen gelten zu können, was sich uns in der Natur als Temperatur kundgibt. Es ist aber das erste und notwendigste Bestimmungsstück der Temperatur, daß beliebige Körper von gleicher Temperatur, miteinander in Berührung gebracht, sich keine Wärme, also keine lebendige Kraft der Atombewegungen mitteilen und wir

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[1]) Voranzeige dieser Arbeit Wien. Anz. 3. S. 36. 8. Februar 1866.

Fig. 3 Boltzmann's kinetic model (Boltzmann 1866, frontispiece and p. 9). Source: BnF Gallica (public domain)

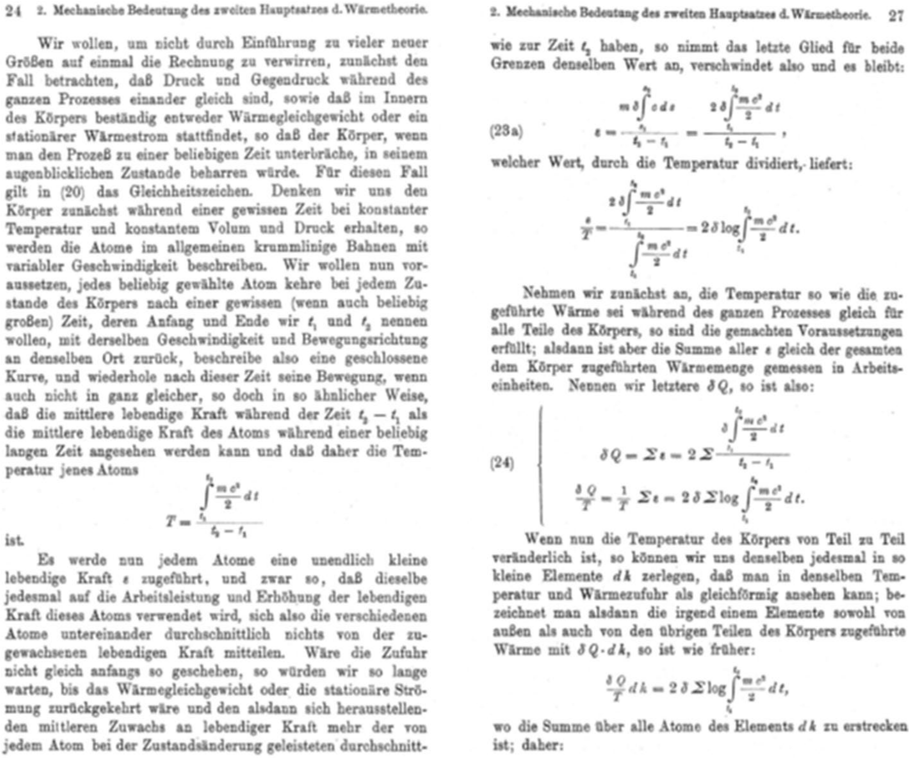
seminal historical documents. As for Boltzmann we will consider the papers: a) Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie (Boltzmann 1866) and b) Weitere Studien über Wärmegleichgewicht unter Gasmolekülen (Boltzmann1872). As for Gibbs we will analyse: On the Equilibrium of Heterogeneous Substances (Gibbs 1906) and The Introduction to statistical mechanics (Gibbs 1902).

Boltzmann's kinetic model, 1866

In few words, Boltzmann's kinetic model—as developed in 1866 paper (Boltzmann 1866)—serves to attain a mathematical expression for the temperature and the heat exchanged by a gaseous system in terms of the kinetic energy of the atoms (or molecules) constituting the system. Boltzmann's final aim is to write–in mechanical (or better kinetic) terms—the second law of Clausius in the case of cyclic processes, corresponding to the following inequality:

$$\int \frac{\delta Q}{T} \leq 0 \tag{21}$$

This attainment would represent the necessary step to attempt a demonstration of the second law, which will be accomplished in 1872 after the well-known H-theorem. We will retrace the main logical steps of such cognitive process, from the foundations of the kinetic



24 2. Mechanische Bedeutung des zweiten Hauptsatzes d. Wärmetheorie.

Wir wollen, um nicht durch Einführung zu vieler neuer Größen auf einmal die Rechnung zu verwirren, zunächst den Fall betrachten, daß Druck und Gegendruck während des ganzen Prozesses einander gleich sind, sowie daß im Innern des Körpers beständig entweder Wärmegleichgewicht oder ein stationärer Wärmestrom stattfindet, so daß der Körper, wenn man den Prozeß zu einer beliebigen Zeit unterbräche, in seinem augenblicklichen Zustande beharren würde. Für diesen Fall gilt in (20) das Gleichheitszeichen. Denken wir uns den Körper zunächst während einer gewissen Zeit bei konstanter Temperatur und konstantem Volum und Druck erhalten, so werden die Atome im allgemeinen krummlinige Bahnen mit variabler Geschwindigkeit beschreiben. Wir wollen nun voraussetzen, jedes beliebig gewählte Atom kehre bei jedem Zustande des Körpers nach einer gewissen (wenn auch beliebig großen) Zeit, deren Anfang und Ende wir t_1 und t_2 nennen wollen, mit derselben Geschwindigkeit und Bewegungsrichtung an denselben Ort zurück, beschreibe also eine geschlossene Kurve, und wiederhole nach dieser Zeit seine Bewegung, wenn auch nicht in ganz gleicher, so doch in so ähnlicher Weise, daß die mittlere lebendige Kraft während der Zeit $t_2 - t_1$ als die mittlere lebendige Kraft des Atoms während einer beliebig langen Zeit angesehen werden kann und daß daher die Temperatur jenes Atoms

$$T = \frac{\int_{t_1}^{t_2} \frac{m c^2}{2} dt}{t_2 - t_1}$$

ist.

Es werde nun jedem Atome eine unendlich kleine lebendige Kraft ε zugeführt, und zwar so, daß dieselbe jedesmal auf die Arbeitsleistung und Erhöhung der lebendigen Kraft dieses Atoms verwendet wird, sich also die verschiedenen Atome untereinander durchschnittlich nichts von der zugewachsenen lebendigen Kraft mitteilen. Wäre die Zufuhr nicht gleich anfangs so geschehen, so würden wir so lange warten, bis das Wärmegleichgewicht oder die stationäre Strömung zurückgekehrt wäre und den alsdann sich herausstellenden mittleren Zuwachs an lebendiger Kraft mehr der von jedem Atom bei der Zustandsänderung geleisteten durchschnitt-

2. Mechanische Bedeutung des zweiten Hauptsatzes d. Wärmetheorie. 27

wie zur Zeit t_2 haben, so nimmt das letzte Glied für beide Grenzen denselben Wert an, verschwindet also und es bleibt:

$$\varepsilon = \frac{m \delta \int_{t_1}^{t_2} c\, ds}{t_2 - t_1} = \frac{2 \delta \int_{t_1}^{t_2} \frac{m c^2}{2} dt}{t_2 - t_1}, \tag{23a}$$

welcher Wert, durch die Temperatur dividiert, liefert:

$$\frac{\varepsilon}{T} = \frac{2 \delta \int_{t_1}^{t_2} \frac{m c^2}{2} dt}{\int_{t_1}^{t_2} \frac{m c^2}{2} dt} = 2 \delta \log \int_{t_1}^{t_2} \frac{m c^2}{2} dt.$$

Nehmen wir zunächst an, die Temperatur so wie die zugeführte Wärme sei während des ganzen Prozesses gleich für alle Teile des Körpers, so sind die gemachten Voraussetzungen erfüllt; alsdann ist aber die Summe aller ε gleich der gesamten dem Körper zugeführten Wärmemenge gemessen in Arbeitseinheiten. Nennen wir letztere δQ, so ist also:

$$\left| \begin{aligned} \delta Q &= \Sigma \varepsilon = 2 \Sigma \frac{\delta \int_{t_1}^{t_2} \frac{m c^2}{2} dt}{t_2 - t_1} \\ \frac{\delta Q}{T} &= \frac{1}{T} \Sigma \varepsilon = 2 \delta \Sigma \log \int_{t_1}^{t_2} \frac{m c^2}{2} dt. \end{aligned} \right. \tag{24}$$

Wenn nun die Temperatur des Körpers von Teil zu Teil veränderlich ist, so können wir uns denselben jedesmal in so kleine Elemente dk zerlegen, daß man in denselben Temperatur und Wärmezufuhr als gleichförmig ansehen kann; bezeichnet man alsdann die irgend einem Elemente sowohl von außen als auch von den übrigen Teilen des Körpers zugeführte Wärme mit $\delta Q \cdot dk$, so ist wie früher:

$$\frac{\delta Q}{T} dk = 2 \delta \Sigma \log \int_{t_1}^{t_2} \frac{m c^2}{2} dt,$$

wo die Summe über alle Atome des Elements dk zu erstrecken ist; daher:

Fig. 4 Conceptualization of heat and temperature in Boltzmann's kinetic model (Boltzmann 1866, p. 24 and p. 27). Source: BnF Gallica (public domain)

model up to the conclusions attained after the H-theorem. As first, we consider the process of conceptualisation of heat and temperature in mechanical terms (Fig. 4).

Boltzmann's kinetic model leans on the following preliminary assumptions:

1. The model–system is a monoatomic gas. The extension to polyatomic gases is provided later.
2. Each atom follows a closed trajectory; that is to say that after an arbitrary time interval (i.e.: $t_2 - t_1$) it returns to the same place with the same velocity and direction of motion;
3. The motion is assumed in such a way that the average *living force* (i.e.: kinetic energy) during $t_2 - t_1$ is the same as the average *living force* for any length of time.

It is in this theoretical groundwork that Boltzmann introduces the concept of temperature of an atom as the average kinetic energy of that atom in the arbitrary time interval $t_2 - t_1$. In Boltzmann's work we read:

> We want now to assume that every arbitrary atom returns to the same place at the same velocity and direction of motion at every state of the body after a certain (albeit arbitrarily large) time, the beginning and end of which we want to name t_1 and t_2, thus describing a closed curve and repeating its movement after this time, albeit not in the same way, but in such a likely way that the average living force during time $t_2 - t_1$

> can be regarded as the average living force of the atom for any length of time and that therefore the temperature of that atom is:
>
> $$T = \frac{\int_{t_1}^{t_2} \frac{mc^2}{2} dt}{t_2 - t_1}. \tag{22}$$
>
> (Boltzmann 1866, p. 24; authors' translation).

This definition of the temperature is the conceptual opening through which Clausius' second law can be expressed in term of atoms' kinetic energy as Boltzmann makes explicit in the following excerpt:

> The obtained concept of temperature allows us to immediately move on to the proof of the second principle of mechanical heat theory, that is, the same one that was obtained in its most general form established for the first time by Clausius.[24]
>
> $$\int \frac{dQ}{T} \leq 0 \tag{23}$$
>
> (Boltzmann 1866, p. 23; authors' translation).

For the sake of more simplicity in the calculations, Boltzmann assumes another approximation. He considers that the process runs in a physical condition that would approximate the reversibility. It is interesting that he specifies this state by considering, as first, that throughout the process pressure and back pressure are the same. This physical requirement recalls the quasi-static state, used in contemporary theoretical thermodynamics to approximate the reversibility. As for as thermal conditions are concerned, he does not mention the temperature. Instead, he outlines a stationary flux of heat. Both assumptions are such that if the process is whatever perturbed, the system maintains its state: that is to say that the system lays into a state of equilibrium. In Boltzmann's work we read:

> In order not to complicate the calculation by introducing too many new variables at once, we first want to look at the case that pressure and back pressure are the same throughout the process, and that within the body there is a constant thermal equilibrium or a stationary flux of heat, so that if the process were perturbed at any time, the body would remain in its present state. In this case, the equal sign applies in Eq. (20) [23[25]].
> (Boltzmann 1866, p. 24; authors' translation).

The conceptualization of heat inside Boltzmann's kinetic model leans on the introduction of an infinitesimal quantity ε, that represents a kinetic energy. A value of such quantity is associated to each constituent atom. Consequently, for a given system, this quantity has a discrete set of values, one for each constituent atom. Mathematically, ε is defined as follows:

---

[24] In current notation this integral should be written as: $\oint \frac{\delta Q}{T}$.

[25] In Boltzmann (Boltzmann 1866, p. 24) we read: "Für diesen Fall gilt in (20) das Gleichheitszeichen". Equation 20 corresponds to Equation 23 of our paper.

$$\varepsilon = \frac{1}{t_2 - t_1} 2\delta \int_{t_1}^{t_2} \frac{mc^2}{2} dt \tag{24}$$

where m is the mass of an arbitrary constituent atom and c is its velocity; the script δ represents the differential. It is worth noticing that in this paper Boltzmann used two scripts for the differential: δ and d. In Boltzmann's word the definition of ε reads as follows:

> An infinitely small *living force* ε is now associated to each atom, in such a way that the increment and decrement of the living force of each atom is such that the exchange of living force between different atoms is null, on average. (Boltzmann 1866, p. 24; authors' translation)

This means that within this kinetic model—on average—we do not register any variation of the kinetic energy of atoms. This assumption corresponds to say that the temperature of the system does not vary per effect of collisions between atoms, since the average kinetic energy of any atom (that Boltzmann supposed constant in this framework) corresponds, by definition, to the temperature (see Eq. 22). After the definition of such model-system, Boltzmann considers what happens when it undergoes to an infinitesimal thermodynamic process. In a first step, the temperature is considered the same for all the parts of the system and the infinitesimal heat exchanged towards the system (δQ) is assumed to be uniformly supplied. In this case, Boltzmann defines the heat supplied, δQ, as the sum of all ε as we can read in the following except:

> If we first assume that the temperature and the heat supplied throughout the process is the same for all parts of the body, such that all the conditions that we established before hold true; then, the sum of all ε is equal to the total amount of heat supplied to the body, which is measured in mechanical units. (Boltzmann 1866, p. 24; authors' translation)

By using the definition of ε (see Eq. 24), δQ can be mathematically expressed as follows:

$$\delta Q = \Sigma\varepsilon = 2\Sigma \frac{1}{t_2 - t_1} \delta \int_{t_1}^{t_2} \frac{mc^2}{2} dt \tag{25}$$

where the index of the sum Σ runs over all the atoms of the system. This latter expression, together with the definition of the temperature of an atom given by Eq. (22), allows writing a mathematical expression for $\frac{\delta Q}{T}$. We have:

$$\frac{\delta Q}{T} = \frac{1}{T}\Sigma\varepsilon = 2\delta\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt \tag{26}$$

The second step is to extend this equation to the case in which the temperature and the heat exchanged are not uniform throughout the system. In such case, the system can be always divided into small volume elements dk in which the temperature and thermal exchange are the same for all parts of dk. Hence, the heat supplied to any volume elements will be $\delta Q \cdot dk$ as we can read in Boltzmann's work:

> If the temperature of the system varies from one part to another, we can always divide the system into small elements that can be considered as characterized by the same temperature and the same heat exchange; by indicating with $\delta Q \cdot dk$ the heat supplied to any volume elements, both from the exterior and from the other part of the system, we have:

$$\frac{\delta Q}{T} dk = 2\delta\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt \tag{27}$$

(Boltzmann 1866, p. 27; authors' translation).

In this latter expression (27), the index of the sum Σ runs over all the atoms of one volume element dk. By integrating the left side over all the system and by running the sum, on the right side, over all the atoms of the system, we obtain:

$$\int \frac{\delta Q}{T} dk = 2\delta\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt \tag{28}$$

For the sake of clarity, we underline that:

1. The integral in the left side of the Eq. (28) is with respect dk, and not δQ;
2. The index of the sum Σ (in Eq. 28) runs over all the atoms of the system, whilst in the previous Eq. (27) the same script Σ represents a sum whose index runs over all the atoms of the small volume dk. Boltzmann does not make it explicit in the mathematical expressions; he specifies this difference in the sum only in the text.

By integrating both members of Eq. (28) with respect to δ, we obtain:

$$\iint \frac{\delta Q}{T} dk = 2\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt + C \tag{29}$$

where the double integral at the first member corresponds to the integral that we find in Clausius' second law for cyclic processes. Hence, Eq. (29) offers a mathematical expression of Clausius' integral $\oint \frac{\delta Q}{T}$ in terms of the kinetic energy of the constituent atoms and constitutes the base for Boltzmann to attempt proving the second law for cyclic processes. This proof would translate into showing that the quantity

$$2\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt + C \tag{30}$$

can always decrease, except in case of reversibility where it zeros. Boltzmann attempted proving it in his 1872 paper in which he developed the famous H-theorem[26] that we analyze in the next section.

Boltzmann's *H*-theorem, 1872

By introducing Boltzmann's H-theorem, Cerciniani wrote:

> Boltzmann not only showed that the equation bearing his name admits Maxwell's distribution as an equilibrium solution, but he also gave a heuristic proof that it is the only possible one. To this end he introduced a quantity, which he denoted by E and later (as here) denoted by H, defined in terms of the molecular velocity distribution. He then demonstrated that as a consequence of this equation, this function

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[26] The *H* is the Greek capital letter *eta*—traditionally used for entropy.

> must always decrease in an isolated system or, at most, remain constant, the latter case occurring only if a state of statistical equilibrium prevails. His result is usually quoted as the "H-theorem" and indicates that H must be proportional to minus the entropy. (Cerciniani 1998, p. 96)

Boltzmann's H-theorem makes explicit the irreversible nature of the quantity E (or H), which always decreases in time (when the gas does not exchange mass and energy with a solid boundary). This result seems to be in conflict with the fact the molecules constituting the gas follow the laws of classical mechanics, which are time-reversible (Cerciniani 1998, p. 97). By using a molecular gas as a model and by leaning on the theory of probability, Boltzmann succeeded in showing that there was no real conflict between the preferred direction in time stemming from the Second Law and the laws of physics at the molecular level, where there is no preferred direction in time. In the following pages, we propose an unedited epistemological analysis of Boltzmann's H-theorem based on an original reading of his 1872 paper.

In 1872 paper, entitled Further Studies on the Thermal Equilibrium of Gas Molecules[27] (Boltzmann 1872), Boltzmann rebuilds his 1866 kinetic model through a statistical perspective. He frames his reflections by considering that the macroscopic thermodynamic state of a system does not change even if the dynamical states of its constituent molecules vary continuously per effect of the continuous motions affecting those molecules. He goes further by observing that despite this variability at the microscopic level, the laws of behavior of warm bodies remain completely definite. The explanation, which he outlines, recalls two intertwined occurrences: a) the fact that the most random events, when they occur in the same proportions, give the same average value and that b) the molecules of the body are indeed so numerous, and their motion is so rapid, that we can perceive nothing more than average values. It is from these premises that he suggests the use of probability theory to determine those average values. In his work we read:

> Hence, even though the body does not change its state, its individual molecules are always changing their states of motion, and the various molecules take up many different positions with respect to each other. The fact that we nevertheless observe completely definite laws of behavior of warm bodies is to be attributed to the circumstance that the most random events, when they occur in the same proportions, give the same average value. For the molecules of the body are indeed so numerous, and their motion is so rapid, that we can perceive nothing more than average values. One might compare the regularity of these average values with the amazing constancy of the average numbers provided by statistics, which are also derived from processes each of which is determined by a completely unpredictable interaction with many other factors. The molecules are likewise just so many individuals having the most varied states of motion, and it is only because the number of them that have, on the average, a particular state of motion is constant, that the properties of the gas remain unchanged. The determination of average values is the task of probability theory. (Boltzmann 2003, pp. 266)

This renewed kinetic theory is built up by modelling a gaseous system as a set of many material points (representing the constituent molecules) moving into a container. For the most of time, these points move following a linear uniform motion. When the molecules

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[27] Original title *Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen.*

interact, they do it by couple as elastic spheres. The interactions between the molecules and the walls of the container are elastic too. Boltzmann makes explicit these details of the model as follows:

> I begin by defining the problem precisely again. Suppose therefore that we have a space R in which are found many gas molecules. Each molecule is a simple point mass, which moves in the way already described. During the largest part of the time, it moves in a straight line with uniform velocity. Two molecules interact only when they come very close together. The law of the force that acts during collisions must of course be given. However, I will not make any restrictive assumptions about this force law. Perhaps the two molecules rebound from each other like elastic spheres; perhaps any other force law may be given. As for the wall of the container that encloses the gas, I will assume that it reflects the molecules like elastic spheres. Any arbitrary force law would lead to the same formulae. However, it simplifies the matter if we make this special assumption about the container. We now set ourselves the following problem: suppose that initially ($t = 0$) the position, velocity, and velocity direction of each molecule is given. (Boltzmann 2003, pp. 266–267).

It is interesting that Boltzmann develops the subsequent calculations by using the kinetic energy of the molecules instead of their velocity. We think that this choice is relevant for several reasons; for example, one is that kinetic energy is a *strictly positive* quantity. Conversely, other authors—for example—preferred to transpose Boltzmann's theorem by using the velocity:

> Actually Boltzmann formulated the discussion in terms of a distribution function over kinetic energy rather than velocity. I have transposed this into the latter, nowadays more common formulation. (Uffink 2007, Ft., p. 964).

Nevertheless, Boltzmann clearly says:

> For the following it will be better to use the kinetic energy of a molecule rather than its velocity. We shall now do this. Let x be the kinetic energy of our gas molecule, so that $x = \frac{mv^2}{2}$. R is the total space in which our gas is enclosed. We construct inside this space R a smaller space called r, whose shape is completely arbitrary but whose volume will be equal to one. (Boltzmann 2003, pp. 267–268).

It is from this premises that he settles the definition of distribution function of kinetic energy $f(x, t)$ as follows:

> The number of molecules in the space r whose kinetic energy at time t lies between x and $x + dx$ I will call $f(x, t)dx$. (Boltzmann 2003, p. 268).

The first important demonstration that we can read in this treatise is that if the distribution of kinetic energy is given by:

$$f(x, t) = C\sqrt{x}e^{-hx} \tag{31}$$

then it holds true that $\partial f(x, t)/\partial t = 0$, that is to say that the distribution of kinetic energy does not vary in the course of time. We read:

> If the distribution of states at any time is determined by the formula 16a [20[28]], then $\partial f(x,t)/\partial t = 0$, i.e. this distribution does not change further in the course of time. This, and nothing else, is what Maxwell proved. However, we shall now consider the problem more generally. We shall assume that the distribution of kinetic energy is initially a completely arbitrary one, and we shall ask ourselves how it changes in the course of time. (Boltzmann 2003, p. 280).

To generalize this statement to the case wherein the initial distribution of kinetic energy is arbitrary, Boltzmann introduces the following new quantity:

$$E = \int_0^\infty f(x,t)\left\{ \log\left[\frac{f(x,t)}{\sqrt{x}}\right] - 1 \right\} dx \tag{32}$$

and demonstrates that its derivative with respect time can never be positive and it zeroes when

$$f(x,t) = C\sqrt{x}e^{-hx} \tag{33}$$

More precisely, he wrote:

> We shall first give the proof of a theorem which forms the basis of our present investigation: the theorem that the quantity
>
> $$E = \int_0^\infty f(x,t)\left\{ \log\left[\frac{f(x,t)}{\sqrt{x}}\right] - 1 \right\} dx \tag{34}$$
>
> can never increase, when the function$f(x,t)$ that occurs in the definite integral satisfies the differential equation (§).[29] (Boltzmann 2003, p. 280).

The detailed analysis of this demonstration has already been object of numerous distinguished papers (Uffink; Sands and Dunning-Davies; Villani; Frigg 2008, Cerciniani 1998) and it is out of the scope of the present work. Conversely, we focus on the conclusions of Boltzmann' reasoning. We read:

> It has thus been rigorously proved that, whatever may be the initial distribution of kinetic energy, in the course of a very long time it must always necessarily approach the one found by Maxwell. The procedure used so far is of course nothing more than a mathematical artifice employed in order to give a rigorous proof of a theorem whose exact proof has not previously been found. It gains meaning by its applicability to the theory of polyatomic gas molecules. There one can again prove that a certain quantity E can only decrease as a consequence of molecular motion, or in a limiting case can remain constant. (Boltzmann 2003, p. 291)

From the introduction of 1866 paper, we know that the actual *interest zone* of Boltzmann lays in the search for a demonstration of Clausius' second law for cyclic process. This is made explicit also in 1872 paper as follows:

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[28] It corresponds to Eq. (20) of this paper.

[29] For the sake of completeness, the differential equation is:
$$\frac{\partial f(x,t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi,t)}{\sqrt{\xi}}\frac{f(x+x'-\xi,t)}{\sqrt{x+x'-\xi}} - \frac{f(x,t)}{\sqrt{x}}\frac{f(x',t)}{\sqrt{x'}}\right]\sqrt{xx'}\psi(x,x',\xi)dx'd\xi.$$

> One can also prove that for the atomic motion of a system of arbitrarily many material points there always exists a certain quantity which, in consequence of any atomic motion, cannot increase, and this quantity agrees up to a constant factor with the value found for the well-known integral $\int \frac{dQ}{T}$ in my paper[30] on the "Analytical proof of the 2nd law, etc.". (Boltzmann 2003, p. 291, author's quotations marks).

In other words, Boltzmann states that, up to a constant factor, the function E, that he has just proved that cannot increase, agrees with the value of Clausius' integral that he obtained in terms of kinetic energy in his 1866 paper.

It is the value that we have commented in the foregoing section (Eq. 30) and that, for the sake of clarity, we report as the following equality:

$$\oint \frac{\delta Q}{T} = 2\Sigma \log \int_{t_1}^{t_2} \frac{mc^2}{2} dt + C \tag{35}$$

The letter C is used (in the primary source) for an arbitrary constant of integration.

The comparison between these latter quantities—i.e. the function E (Eq. 32) and the value of Clausius' integral (Eq. 30) is not self-evident. In the secondary literature, as far as we know, the correspondence between these quantities was never made explicit.

Nevertheless, we have tried to find a sense to this comparison. The definite integral with respect of time—on the right side of Eq. (35)—gives the kinetic energy of one atom: that by employing the same notation of 1872 paper should be written as x.

Hence, the result given by Eq. (30) can be written as

$$2\Sigma \log \mathrm{x} + C \tag{36}$$

where x is the kinetic energy of an atom and the sum is extended to all the atoms of system. Moreover, Eq. (32) can be rearranged as follows:

$$E = -\frac{1}{2} \int_0^{\infty} \log x f(x,t) dx + \varphi(t) \tag{37}$$

being $\varphi(t)$ the following integral[31]:

$$\varphi(t) = \int_0^{\infty} (\log f(x,t) - 1) f(x,t) dx \tag{38}$$

The integral in Eq. (37) is extended to all the values of kinetic energy and the quantity $f(x,t)dx$ represents the number of molecules with energy x. Hence, the substantial difference between the expressions (36) and (37) is that in (36) there is a sum instead of an integral. Boltzmann demonstrates in this same 1872 paper that the integral can be substituted by a sum. On this base, Boltzmann's statement does not seem out of place. By leaning on this agreement between E and the expression obtained for $\oint \frac{\delta Q}{T}$, Boltzmann argue to have found a demonstration of Clausius' second law for cyclic processes. In Boltzmann works Clausius integral for cyclic processes is written as $\int \frac{dQ}{T}$ instead of $\oint \frac{\delta Q}{T}$. We read:

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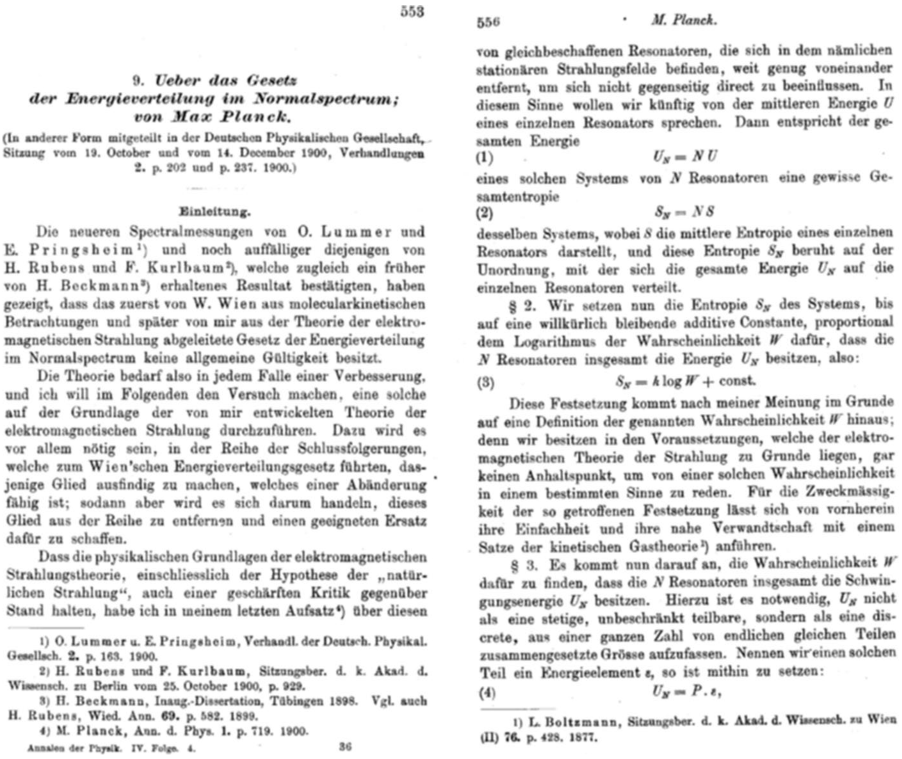
[30] Cfr. Boltzmann (1866).

[31] For sake of brevity/calculus we choose to denote the quantity $\varphi(t)$ which is not included in the primary sources text.

> We have therefore prepared the way for an analytical proof of the second law in a completely different way from those previously investigated. Up to now the object has been to show that $\int \frac{dQ}{T} = 0$[32]for reversible cyclic processes, but it has not been proved analytically that this quantity is always negative for irreversible processes, which are the only ones that occur in nature. The reversible cyclic process is only an ideal, which one can more or less closely approach but never completely attain. Here, however, we have succeeded in showing that $\int \frac{dQ}{T}$ is in general negative, and is equal to zero only for the limiting case, which is of course the reversible cyclic process (since if one can go through the process in either direction, $\int \frac{dQ}{T}$ cannot be negative). (Boltzmann 2003, p. 291).

The H-theorem and its consequences were object of numerous and qualified critics, even during Boltzmann's time. In the secondary literature, there are many commentaries (Villani; Frigg 2008; Uffink; Sands and Dunning-Davies; Cerciniani 1998, etc.). We do not remain further on this subject since it is out of the scope of our research. Instead, we consecrate the next section to Planck's hermeneutical reading of Boltzmann's model that allowed delivering the well-known equation $S = k \log W$ (Fig. 5).



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9. *Ueber das Gesetz der Energieverteilung im Normalspectrum; von Max Planck.*

(In anderer Form mitgeteilt in der Deutschen Physikalischen Gesellschaft, Sitzung vom 19. October und vom 14. December 1900, Verhandlungen 2. p. 202 und p. 237. 1900.)

Einleitung.

Die neueren Spectralmessungen von O. Lummer und E. Pringsheim[1]) und noch auffälliger diejenigen von H. Rubens und F. Kurlbaum[2]), welche zugleich ein früher von H. Beckmann[3]) erhaltenes Resultat bestätigten, haben gezeigt, dass das zuerst von W. Wien aus molecularkinetischen Betrachtungen und später von mir aus der Theorie der elektromagnetischen Strahlung abgeleitete Gesetz der Energieverteilung im Normalspectrum keine allgemeine Gültigkeit besitzt.

Die Theorie bedarf also in jedem Falle einer Verbesserung, und ich will im Folgenden den Versuch machen, eine solche auf der Grundlage der von mir entwickelten Theorie der elektromagnetischen Strahlung durchzuführen. Dazu wird es vor allem nötig sein, in der Reihe der Schlussfolgerungen, welche zum Wien'schen Energieverteilungsgesetz führten, dasjenige Glied ausfindig zu machen, welches einer Abänderung fähig ist; sodann aber wird es sich darum handeln, dieses Glied aus der Reihe zu entfernen und einen geeigneten Ersatz dafür zu schaffen.

Dass die physikalischen Grundlagen der elektromagnetischen Strahlungstheorie, einschliesslich der Hypothese der „natürlichen Strahlung", auch einer geschärften Kritik gegenüber Stand halten, habe ich in meinem letzten Aufsatz[4]) über diesen

1) O. Lummer u. E. Pringsheim, Verhandl. der Deutsch. Physikal. Gesellsch. 2. p. 163. 1900.

2) H. Rubens und F. Kurlbaum, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin vom 25. October 1900, p. 929.

3) H. Beckmann, Inaug.-Dissertation, Tübingen 1898. Vgl. auch H. Rubens, Wied. Ann. 69. p. 582. 1899.

4) M. Planck, Ann. d. Phys. 1. p. 719. 1900.

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556 *M. Planck.*

von gleichbeschaffenen Resonatoren, die sich in dem nämlichen stationären Strahlungsfelde befinden, weit genug voneinander entfernt, um sich nicht gegenseitig direct zu beeinflussen. In diesem Sinne wollen wir künftig von der mittleren Energie U eines einzelnen Resonators sprechen. Dann entspricht der gesamten Energie

$$U_N = N\,U \tag{1}$$

eines solchen Systems von N Resonatoren eine gewisse Gesamtentropie

$$S_N = N\,S \tag{2}$$

desselben Systems, wobei S die mittlere Entropie eines einzelnen Resonators darstellt, und diese Entropie S_N beruht auf der Unordnung, mit der sich die gesamte Energie U_N auf die einzelnen Resonatoren verteilt.

§ 2. Wir setzen nun die Entropie S_N des Systems, bis auf eine willkürlich bleibende additive Constante, proportional dem Logarithmus der Wahrscheinlichkeit W dafür, dass die N Resonatoren insgesamt die Energie U_N besitzen, also:

$$S_N = k \log W + \text{const.} \tag{3}$$

Diese Festsetzung kommt nach meiner Meinung im Grunde auf eine Definition der genannten Wahrscheinlichkeit W hinaus; denn wir besitzen in den Voraussetzungen, welche der elektromagnetischen Theorie der Strahlung zu Grunde liegen, gar keinen Anhaltspunkt, um von einer solchen Wahrscheinlichkeit in einem bestimmten Sinne zu reden. Für die Zweckmässigkeit der so getroffenen Festsetzung lässt sich von vornherein ihre Einfachheit und ihre nahe Verwandtschaft mit einem Satze der kinetischen Gastheorie[1]) anführen.

§ 3. Es kommt nun darauf an, die Wahrscheinlichkeit W dafür zu finden, dass die N Resonatoren insgesamt die Schwingungsenergie U_N besitzen. Hierzu ist es notwendig, U_N nicht als eine stetige, unbeschränkt teilbare, sondern als eine discrete, aus einer ganzen Zahl von endlichen gleichen Teilen zusammengesetzte Grösse aufzufassen. Nennen wir einen solchen Teil ein Energieelement ε, so ist mithin zu setzen:

$$U_N = P \, . \, \varepsilon, \tag{4}$$

1) L. Boltzmann, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien (II) 76. p. 428. 1877.

Fig. 5 Planck's Seminal definition of entropy within the black body radiation theory (Planck 1901, pp. 553 and 556). Source: BnF Gallica (public domain)

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[32] In current notation this integral should be written as: $\oint \frac{\delta Q}{T}$

Planck-Boltzmann's equation, 1901

The formal origin of the equation giving what is known as Boltzmann's entropy is actually due to Max Planck[33] who—in his fundamental work on black body radiation (Planck 1901)—with reference to a system made of N resonators, wrote:

> Now we state that the Entropy of the system S_N, is proportional - up to an additive constant - to the logarithm of the probability *W* for N resonators to have energy equal to U_N, that is to say:
>
> $$S_N = k \log W + const.$$
>
> (Planck 1901, p. 556; Authors' Translation)

Planck's reasoning leading to this equation and its cognitive relationship with Boltzmann's kinetic theory are made explicit in the book *The theory of Heat radiation* (Planck 1914); on this base, we retrace the logical and mathematical steps of this opening, starting from the following assumption:

> Hence, we make the following proposition the foundation of our further discussion: *The entropy of a physical system in a definite state depends solely on the probability of this state*. (Planck 1914 p. 139; author's italic style)

Which mathematically translates into the general expression:

$$S = f(W) \tag{39}$$

where $f(W)$ represents a universal function of the argument W, that is the probability of the state. Subsequently, two independent systems are given.

> […] the first system as any body whatever on the earth and […] the second system as a cavity containing radiation on Sirius, [such that] the probability that the terrestrial body be in a certain state 1 and that simultaneously the radiation in the cavity in a definite state 2 is
>
> $$W = W_1 W_2$$
>
> (Planck 1914, p. 140),

where W_1 and W_2 are the respective probabilities of these systems. Their entropies are then given as $S_1 = f(W_1)$ and $S_2 = f\left(W_2\right)$ respectively.

> But, according to the second principle of thermodynamics, the total entropy of the two systems, which are independent […] of each other, is $S = S_1 + S_2$.
>
> (Planck 1914, p. 140)

Consequently, we have:

$$f\left(W_1 W_2\right) = f\left(W_1\right) + f\left(W_2\right) \tag{40}$$

---

[33] Concerning the influence of Boltzmann kinetic model on Planck's works, Cerciniani comments: "Many historians of science have underlined the circumstance that these discrete models used by Boltzmann led Planck to the discovery of his energy *quanta*." (Cercignani 1998, p. 89).

To determine f from the foregoing functional equation, Planck differentiates both sides of the equation with respect to W_1 and W_2, successively. Namely, by differentiating with respect to W_1, being W_2 constant, he obtains:

$$W_2\dot{f}\left(W_1W_2\right) = \dot{f}\left(W_1\right) \tag{41}$$

Then, by differentiating the foregoing result with respect to W_2, he obtains:

$$\dot{f}\left(W_1W_2\right) + W_1W_2\ddot{f}\left(W_1W_2\right) = 0 \tag{42}$$

that is to say:

$$\dot{f}(W) + W\ddot{f}(W) = 0 \tag{43}$$

The general solution of such second order differential equation is:

$$f(W) = k\log W + const. \tag{44}$$

that, from the initial proposition $S = f(W)$, becomes:

$$S = k\log W + const. \tag{45}$$

This expression, intertwining entropy and probability, contains two constants, k and *const.*, whose meaning and values are clarified as follows:

> The universal constant of integration k is the same for a terrestrial as for a cosmic system, and its value, having been determined for the former, will remain valid for the latter. The second additive constant of integration may, without any restriction as regards generality, be included as a constant multiplier in the quantity W, which here has not yet been completely defined, so that the equation reduces to
>
> $$S = k\log W \text{ (Planck 1914, p.141)}$$

This is the well-known expression of Boltzmann's equation. But what is the ratio that links this result to Boltzmann's kinetic theory? Planck synthetically answers as follows:

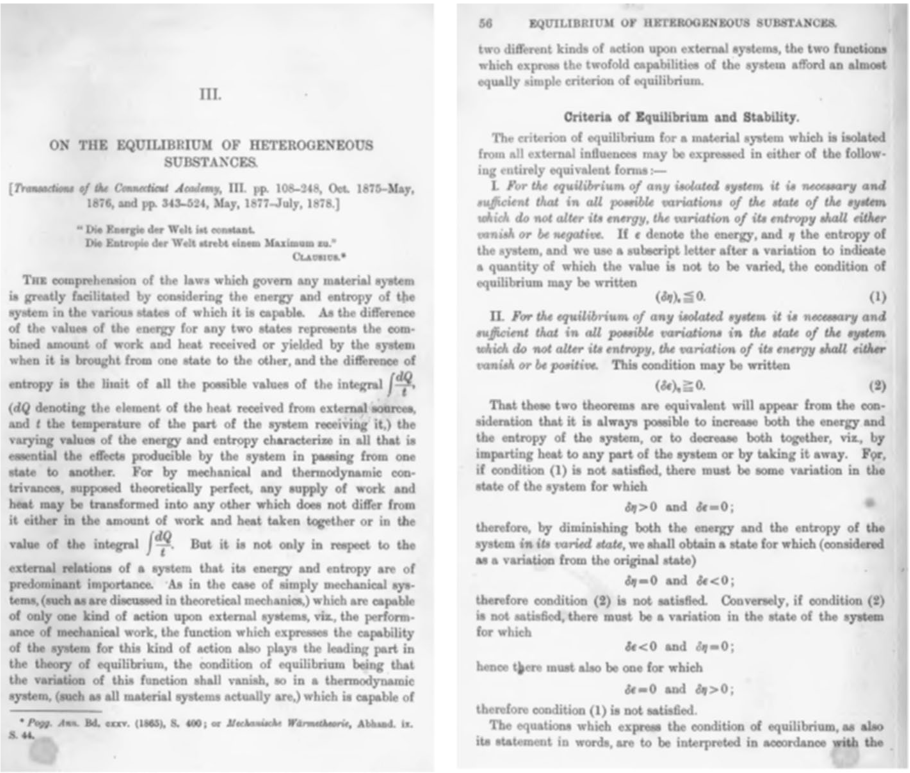
> The logarithmic connection between entropy and probability was first stated by L. Boltzmann in his kinetic theory of gases. Nevertheless, our equation [i.e., $S = k\log W$] differs in its meaning from the corresponding one of Boltzmann in two essential points. Firstly, Boltzmann's equation lacks the factor k, which is due to the fact that Boltzmann always used gram-molecules, not the molecules themselves, in his calculations. Secondly, and this is of greater consequence, Boltzmann leaves an additive constant undetermined in the entropy S as is done in the whole of classical thermodynamics, and accordingly there is a constant factor of proportionality, which remains undetermined in the value of the probability W. (Planck 1914, p. 141).

The thermodynamic entropy *à la* Gibbs, 1875

Another conceptualisation of entropy, embodied inside a truly different context, stems from Willard Gibbs' (1839–1903) geometrical theory of chemical equilibrium. In particular, in Gibbs we find an epistemological extension of Clausius' Second Law (Clausius 1867, 1872; Gibbs 1892, 1899, 1906; Pellegrino et al. 2015, 2016; Pellegrino and Cerruti 2016) to model *the equilibrium of heterogeneous systems* (i.e. *chemical equilibrium*). More specifically, Gibbs develops his model by combining thermodynamic arguments, emerging from Clausius theory, with the methods of analytical geometry (Fig. 6).

His foundational assumption is that:

> […] the leading thermodynamic properties of a fluid are determined by the relations which exist between the volume, pressure, temperature, energy, and entropy of a given mass of the fluid in a state of thermodynamic equilibrium. (Gibbs 1906, p. 33).



III.

ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES.

[*Transactions of the Connecticut Academy*, III. pp. 108–248, Oct. 1875–May, 1876, and pp. 343–524, May, 1877–July, 1878.]

"Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu."
CLAUSIUS.*

THE comprehension of the laws which govern any material system is greatly facilitated by considering the energy and entropy of the system in the various states of which it is capable. As the difference of the values of the energy for any two states represents the combined amount of work and heat received or yielded by the system when it is brought from one state to the other, and the difference of entropy is the limit of all the possible values of the integral $\int\frac{dQ}{t}$, (dQ denoting the element of the heat received from external sources, and t the temperature of the part of the system receiving it,) the varying values of the energy and entropy characterize in all that is essential the effects producible by the system in passing from one state to another. For by mechanical and thermodynamic contrivances, supposed theoretically perfect, any supply of work and heat may be transformed into any other which does not differ from it either in the amount of work and heat taken together or in the value of the integral $\int\frac{dQ}{t}$. But it is not only in respect to the external relations of a system that its energy and entropy are of predominant importance. As in the case of simply mechanical systems, (such as are discussed in theoretical mechanics,) which are capable of only one kind of action upon external systems, viz., the performance of mechanical work, the function which expresses the capability of the system for this kind of action also plays the leading part in the theory of equilibrium, the condition of equilibrium being that the variation of this function shall vanish, so in a thermodynamic system, (such as all material systems actually are,) which is capable of

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* *Pogg. Ann.* Bd. cxxv. (1865), S. 400; or *Mechanische Wärmetheorie*, Abhand. ix. S. 44.

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two different kinds of action upon external systems, the two functions which express the twofold capabilities of the system afford an almost equally simple criterion of equilibrium.

Criteria of Equilibrium and Stability.

The criterion of equilibrium for a material system which is isolated from all external influences may be expressed in either of the following entirely equivalent forms:—

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.* If ϵ denote the energy, and η the entropy of the system, and we use a subscript letter after a variation to indicate a quantity of which the value is not to be varied, the condition of equilibrium may be written

$$(\delta\eta)_\epsilon \leqq 0. \tag{1}$$

II. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in 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

$$(\delta\epsilon)_\eta \geqq 0. \tag{2}$$

That these two theorems are equivalent will appear from the consideration that it is always possible to increase both the energy and the entropy of the system, or to decrease both together, viz., by imparting heat to any part of the system or by taking it away. For, if condition (1) is not satisfied, there must be some variation in the state of the system for which

$$\delta\eta>0 \text{ and } \delta\epsilon=0;$$

therefore, by diminishing both the energy and the entropy of the system *in its varied state*, we shall obtain a state for which (considered as a variation from the original state)

$$\delta\eta=0 \text{ and } \delta\epsilon<0;$$

therefore condition (2) is not satisfied. Conversely, if condition (2) is not satisfied, there must be a variation in the state of the system for which

$$\delta\epsilon<0 \text{ and } \delta\eta=0;$$

hence there must also be one for which

$$\delta\epsilon=0 \text{ and } \delta\eta>0;$$

therefore condition (1) is not satisfied.

The equations which express the condition of equilibrium, as also its statement in words, are to be interpreted in accordance with the

Fig. 6 Gibbs geometrical model and the criteria of thermodynamic equilibrium. (Gibbs 1906, I, pp. 55 and 56). Source: http://www.archive.org (public domain)

The fundamental relation between these thermodynamic variables is given by the differential equation $d\varepsilon = td\eta - pdv$, where v, p, t, ε and η denote volume, pressure, absolute temperature, energy, and entropy, respectively. By using the current thermodynamic notation, this equation reads as:

$$dU = TdS - pdV$$

that holds true in the case of reversible processes and pV-work. It derives from Clausius equations $dU = \delta Q - pdV$ and $dS = \frac{\delta Q}{T}$. Gibbs comments this fundamental relation as follows:

> This equation evidently signifies that if ε be expressed as function of v and η, the partial differential coefficients of this function taken with respect to v and to η will be equal to $-p$ and to t respectively. (Gibbs 1906, p. 2).

In other words, a function of two variables $\varepsilon = \varepsilon(\eta, v)$ can be obtained from the above differential equation, whose differential coefficients are $-p$ and t. With reference to a Cartesian three-fold space where the (X, Y, Z) coordinates are made univocally correspond to (v, η, ε) values, the two-variables-function $\varepsilon = \varepsilon(\eta, v)$ is represented by a surface that Gibbs referred to as the *thermodynamic surface*. The geometrical properties of this surface allowed delivering a general criterion establishing the conditions of stability of a thermodynamic system and consequently the direction of spontaneous thermodynamic transformations. That is:

> The criterion of equilibrium for a material system, which is isolated from all external influences, may be expressed in either of the following entirely equivalent forms:
> 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.* If ε denote the energy, and η the entropy of the system, and we use a subscript letter after a variation to indicate a quantity of which the value is not to be varied, the condition of equilibrium may be written:
>
> $$(\delta\eta)_\varepsilon \le 0$$
>
> II *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in 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:
>
> $$(\delta\varepsilon)_\eta \ge 0.$$
>
> (Gibbs 1906, p. 56)

Therefore, the equilibrium state of an isolated *material system*, undergoing a change at constant energy, corresponds to the maximum entropy state. Vice versa, at constant entropy conditions, the equilibrium is achieved when minimum energy is attained. This dual principle is valid for all thermodynamic systems, including those with variable chemical composition.

In conclusion, Gibbs restraints his theory to reversible processes. This strong approximation, allowed him to build up a geometrical model that encapsulates, in a three-dimensional surface, all the thermodynamic properties of the system. The problem of irreversibility and the fact that real processes are inherently irreversible has been widely treated in our previous paper (Pisano et al. 2019) and is out of the scope of the present research.

Gibbs' statistical entropy, 1902

Gibbs grounded his statistical model on a new key concept, the *ensemble* that corresponds to a theoretical construction representing a thermodynamic system by means of a set of theoretical copies of the system in the same thermodynamic state, each one differing only for the dynamic state (i.e. positions and moments distribution of the constituent particles). This approach allows having a broader view; that is to say that the model does not limit to follow a particular system through the succession of its dynamical configurations. It determines how the copies of the system are distributed among the possible configurations and velocities. We read:

> For some purposes, however, it is desirable to take a broader view of the subject. We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity. (Gibbs 1902, p. vii)

In other words, whereas Boltzmann restricts the application of statistical arguments to systems made of a great number of identical constituents, Gibbs—by introducing the concept of *ensemble*—de facto applies the statistical reasoning to a *sample* consisting of *a great number of thermodynamic systems,* having the same thermodynamic state and mutually differing for their dynamic states (i.e. positions and momenta distribution of the constituent particles). This brainchild allows Gibbs to extend statistical mechanics to the description of systems that, at least in principle, may include many distinct constituents. Gibbs outlines this possibility as follows:

> Such inquiries have been called by Maxwell statistical. They belong to a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles, and of which Clausius, Maxwell, and Boltzmann are to be regarded as the principal founders. The first inquiries in this field were indeed somewhat narrower in their scope than that which has been mentioned, being applied to the particles of a system, rather than to independent systems. (Gibbs 1902, p. viii)

Hence, with reference to the general case of a system with n degrees of freedom in the formal framework of Hamilton's method—i.e. by writing the equations of motion in terms of generalized coordinates and momenta—the statistical model is built up by considering a set of many copies of the thermodynamic system, having the same *thermodynamic state* and mutually differing for their *dynamic states*.

> Let us imagine a great number of independent systems, identical in nature, but differing in phase, that is, in their condition with respect to configuration and velocity. The forces are supposed to be determined for every system by the same law, being functions of the coordinates of the system $q_1 ... q_n$, either alone or with the coordinates $a_1, a_2, etc.$ of certain external bodies. (Gibbs 1902, p. 5).

A coefficient of probability P is then associated to each system of the ensemble. It is in this groundwork that the condition of statistical equilibrium is defined as follows:

> Let us now give our attention to the statistical equilibrium of ensembles of conservation systems, especially to those cases and properties which promise to throw light on the phenomena of thermodynamics. The condition of statistical equilibrium may be expressed in the form
>
> $$\sum\left(\frac{dP}{dp_1}\dot{p}_1+\frac{dP}{dq_1}\dot{q}_1\right)=0 \tag{46}$$
>
> where P is the coefficient of probability, or the quotient of the density-in-phase by the whole number of systems. To satisfy this condition, it is necessary and sufficient that P should be a function of the p's and q's (the momenta and coordinates) which does not vary with the time in a moving system. (Gibbs 1902, p. 32)

To disclose the cryptic mathematical expression on the right side of Eq. 35, it is necessary to make explicit the very special notation that Gibbs used in this treatise. The key can be found in chapter one (Gibbs 1902, p. 8), where the variation of the density-in-phase is discussed. The first member corresponds to the time derivative of P and, mathematically, we can write:

$$\left(\frac{dP}{dt}\right)_{p,q}=-\sum\left(\frac{dP}{dp_1}\dot{p}_1+\frac{dP}{dq_1}\dot{q}_1\right) \tag{47}$$

Hence, Gibbs' statistical equilibrium corresponds to the condition wherein the probability P does not vary with time. Furthermore, Gibbs specifies that in all considered cases, the energy of the system or any function of the energy satisfies the condition of statistical equilibrium. We read:

> In all cases which we are now considering, the energy, or any function of the energy, is such a function. $P = func.(\varepsilon)$ will therefore satisfy the equation, as indeed appears identically if we write it in the form
>
> $$\sum\left(\frac{dP}{dp_1}\frac{d\varepsilon}{dp_1}-\frac{dP}{dq_1}\frac{d\varepsilon}{dq_1}\right)=0 \tag{48}$$
>
> (Gibbs 1902, p. 32).

The probability P, beside the condition of statistical equilibrium, have to satisfy further conditions:

> There are, however, other conditions to which P is subject, which are not so much conditions of statistical equilibrium, as conditions implicitly involved in the definition of the coefficient of probability, whether the case is one of equilibrium or not. These are: that P should be single-valued, and neither negative nor imaginary for any phase, and that expressed by […]
>
> $$\underset{phase}{\overset{all}{\int}}\ldots\ldots\int P dp_1 \quad dq_n = 1 \tag{49}$$
>
> (Gibbs 1902, pp. 32–33).

In other words, P should be single-valued, not imaginary, not negative and its integral over all the phases should be unitary. Gibbs identified a functional form for P as the simplest one that satisfies all the foregoing requisites. It is an exponential function of the energy that he defines as follows:

> The distribution represented by
>
> $$\eta = \log P = \frac{\psi - \varepsilon}{\Theta}$$
>
> or
>
> $$P = e^{\frac{\psi - \varepsilon}{\Theta}}$$
>
> where Θ and ψ are constants, and Θ positive, seems to represent the most simple case conceivable, since it has the property that when the system consists of parts with separate energies, the laws of the distribution in phase of the separate parts are of the same nature, a property which enormously simplifies the discussion, and is the foundation of extremely important relations to thermodynamics. (Gibbs 1902, p. 33).

This particular distribution is named canonical and the ensemble distributed in this manner is canonically distributed. We read:

> When an ensemble of systems is distributed in phase in the manner described, i.e. when the index of probability is a linear function of the energy, we shall say that the ensemble is *canonically distributed*, and shall call the divisor of the energy Θ the *modulus* of distribution. (Gibbs 1902, pp. 33–34; author's italic style).

At this step of the reasoning η is a statistical function without any physical meaning. The only variable with physical meaning is ε—the energy. Gibbs attempts to attribute a meaning to η by comparison with the thermodynamic relation between the energy, temperature and entropy of the body. We finalize this section by retracing the main steps of Gibbs' reasoning. We can identify the key point of this logical process in the following definition of the average value of whatever quantity in the canonically distributed ensemble:

> Now the average value in the ensemble of any quantity (which we shall denote in general by a horizontal line above the proper symbol) is determined by the equation
>
> $$\bar{u} = \int_{phase}^{all} \dots \dots \int u e^{\frac{\psi - \varepsilon}{\Theta}} dp_1 \qquad dq_n = 1$$
>
> (Gibbs 1902, p. 44).

On this base, Gibbs—through a long mathematical reasoning that we omit—obtains the following equation intertwining the average value of energy $\bar{\varepsilon}$ with the average value of the statistical variables defined in the model:

$$d\bar{\varepsilon} = -\Theta d\bar{\eta} - \bar{A}_1 da_1 - \bar{A}_2 da_2 \tag{50}$$

Θ is the modulus, $\bar{\eta}$ is the distribution and a_1, a_2, … are external coordinates that we can neglect, since we consider the case of a closed system. Hence, we can simplify Eq. (50) into:

$$d\overline{\varepsilon} = -\Theta d\overline{\eta} \tag{51}$$

> By commenting equation (50), Gibbs writes:
> This equation, if we neglect the sign of averages, is identical in form with the thermodynamic equation
>
> $$d\eta = \frac{d\varepsilon + A_1 da_1 + A_2 da_2 + etc.}{T} \tag{52}$$
>
> Or
>
> $$d\varepsilon = T d\eta - A_1 da_1 - A_2 da_2 - etc., \tag{53}$$
>
> which expresses the relation between the energy, temperature, and entropy of a body in thermodynamic equilibrium, and the forces which it exerts on external bodies,—a relation which is the mathematical expression of the second law of thermodynamics for reversible changes. (Gibbs 1902, p. 44)

In case of closed system, Equation (51) reduces to $d\varepsilon = \mathrm{T}d\eta$; hence:

> The modulus in the statistical equation corresponds to temperature in the thermodynamic equation, and the average index of probability with *its sign reversed* corresponds to entropy. (Gibbs 1902, p. 44)

In other words the modulus corresponds to temperature and that the average index of probability corresponds to entropy, even if with the sign reversed. But this is just an analogical attribution. Gibbs does not attribute a physical meaning to that average index of probability $\overline{\eta}$. He openly remarks that thermodynamic entropy is defined up to an arbitrary constant of integration. Its absolute value, as we have previously discussed, cannot be directly obtained from Clausius' equation without leaning on other empiric principles. In Gibbs' work we read:

> But in the thermodynamic equation the entropy (η) is a quantity which is only defined by the equation itself, and incompletely defined in that the equation only determines its differential, and the constant of integration is arbitrary. On the other hand, the ($\overline{\eta}$) in the statistical equation has been completely defined as the average value in a canonical ensemble of systems of the logarithm of the coefficient of probability of phase. (Gibbs 1902, pp. 44–45).

In conclusion Gibbs distribution function $\overline{\eta}$ does not coincide with thermodynamic entropy *tout court* but rather it is the analogical structure intertwining thermodynamic and statistical equations that allows establishing a semantic correspondence between thermodynamic entropy and the foregoing Gibbs' statistical distribution function.

Intermezzo on Gibbs' entropy and Shannon's function

Here we focus our discussion on the similarities and differences between Gibbs' statistical distribution function (currently known as Gibbs' statistical entropy) and Shannon's function, introduced in the context of the Communication theory. For the sake of clarity, we firstly recall the currently used expression for Gibbs' statistical entropy. Gibb's distribution function for a canonically distributed ensemble is mathematically expressed as a logarithmic function of the probability to find, in the ensemble, a given copy of the thermodynamic system into a given energetic state; that is:

$$\overline{\eta} = \log P \tag{54}$$

In current statistical mechanics,[34] Gibbs' entropy is usually expressed as:

$$S = -k_B \sum_i P_i \ln P_i \tag{55}$$

where k_B is the Boltzmann's constant and P_i is the probability to find the system in the state with energy E_i. The sum is extended to all the accessible states.

In 1948, an American electric engineer, Claude Elwood Shannon (1916–2001), published two papers entitled Mathematical Theory of Communication (Shannon 1848) wherein he outlines the bases of the current theory of communication. Within his model, Shannon defines a function whose mathematical expression is:

$$H = -K \sum_i p_i \log p_i \tag{56}$$

and that represents the information exchanged through a communication channel. It is named *entropy*[35] for its *formal similarity with entropy as defined in certain formulation of statistical mechanics* (Shannon 1948, p. 393). Actually, at first glance, this function seems to superpose Gibbs' one (Eq. 55). However, this impression is misleading. To make explicit the differences, we briefly recall some foundations of Shannon's theory.

The following flow chart of Fig. 7 provides a very general description of a *communication process*.

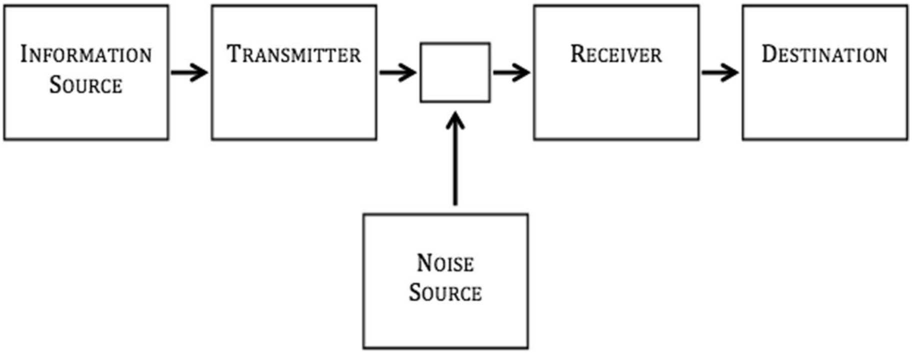

Fig. 7 Flow chart representing a communication system; adapted from Shannon (Shannon 1948, p. 381)

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[34] Cfr. Hill (1986).

[35] Actually, Shannon refers to this same entity either as *information* or *uncertainty*.

At the beginning, a *source of information* generates a message to transmit. For the sake of clarity, let us imagine that we wish to transmit the word “DEPOSITO”.

The message can be represented in the form of an alphanumeric string, as a raw vector whose running index i identifies the letters’ position (Table 1). The alphanumeric string—i.e. the 8-letters-sequence of the word DEPOSITO—is translated into a sequence of signals (electrical or electromagnetic) and then transmitted. Through a communication channel, the signal gets to the receiver. During transmission, external perturbations (e.g. noise sources) may alter the signals. After decoding (i.e. back translation of the signals’ sequence into an alphanumeric string), the message gets to destination. By simplifying, it can be said that the overall communication process has to be designed and achieved by minimizing the source of noise in order to assure that the alphanumeric string that gets to destination contains the same information that was transmitted.

Table 1 Example conceived to clarify the meaning of Shannon function

D	E	P	O	S	I	T	O	Alphanumeric string reporting the message
1	2	3	4	5	6	7	8	i (letter position index)

Shannon’s function serves to handle both the pieces of *information* transmitted and the uncertainty by which the message arrives at destination—*uncertainty* that is mainly due to the source of noise that perturbs the communication process.

With reference to the example of Table 1, the running index of the sum identifies the letters’ position inside the alphanumeric string representing the message and p_i is the probability to find a particular alphanumeric script in position i. For example—in the case of the word DEPOSITO—p_2 is the probability to find “E” in position 2. K is a positive constant chosen in order to make the dimensions of the H function correspond to the number of bits. In Shannon’s words this definition reads as follows:

Theorem 2 The only H satisfying the three above assumptions is of the form:

$$H = -K \sum_i p_i \log p_i$$

where K is a positive constant.

> This theorem and the assumptions required for its proofs are in no way necessary for the present theory. It is given chiefly to lend a certain plausibility to some of our later definitions. The real justification of these definitions, however, will reside in their implications.
> Quantities of the form $H = -K \sum_i p_i \log p_i$ (the constant K merely amounts to a choice of a unit of measure) play a central role in information theory as measure of information, choice and uncertainty. The form of H will be recognized as that of entropy as defined in certain formulations of statistical mechanics where p_i is the probability of a system being in cell i of its phase space. H is then, for exam-

> ple, the H in Boltzmann's famous H theorem. We shall call $H = -K\sum_i p_i \log p_i$ the entropy of the set of probabilities $p_1 \ldots p_n$.
> (Shannon 1948, p. 393)

This concise description of Shannon's H function is detailed enough to highlight that this latter is not an entropy *stricto sensu*. In fact, the dimension of H is the number of bits and not Joule (Pisano, Vincent, Dolenc and Ploj-Virtič 2020) per Kelvin (Smith and Wise 1989)—as it is the case of thermodynamic or statistical entropy. In Shannon's function the logarithm is in base 2 whilst in Gibb's entropy we find the natural logarithm. In Gibbs the constant is Boltzmann's constant and in Shannon K is an arbitrary positive constant. The last but not least, P_i is the probability to find a system of the Gibbs' ensemble in the state with energy ε_i. In Shannon's function, p_i is the probability to find an alphanumeric script in the position *i.*

In conclusion, Shannon and Gibbs entropies are different on both formal and ontological levels. A piece of information or an uncertainty ontologically belong to truly different context with respect to the Gibbs' statistical entropy, which (as previously discussed) is in analogical relation with the notion of thermodynamic entropy.

Nevertheless, it is very interesting that Shannon mentions the similarity of his function with statistical entropy when he decided to name it such. In fact, this may suggest the scientific roots of Shannon's theory. This cognitive circumstance recalls a recent original hypothesis on the scientific roots of Sadi Carnot's cycle. In that case the analogy—that would have driven Sadi Carnot—is established with the electric circuit in Alessandro Volta's battery. On this matter we read:

> Sometimes, not always, in the history of science, a process of scientific knowledge advances with help from the assumptions that one has previously acquired from another domain. (Gillispie and Pisano 2014, 2nd ed., p. 227).

Conclusions

In this paper we have outlined three major conceptual steps of the history of the entropy, starting from its thermodynamic definition as defined by Clausius up its uses in the statistical mechanics. By leaning on the already published results of this research program (Pisano et al. 2019) we have recalled the epistemic value of Clausius' second law. In particular, we have underlined the differentiation of Clausius' approach to handle cyclic and not-cyclic processes and that the definition of entropy emerged when Clausius finally settled the second law for not-cyclic processes.

Historically, Clausius' memoires served as the foundational platform for the development of both statistical theories, authored by Boltzmann and Gibbs. We have detailed the foundations of these theories through a precise analysis of historical documents.

As for Boltzmann, we have retraced the process of conceptualization of the temperature and heat inside his kinetic model and disclosed some aspects of the well-known H-theorem by framing it inside Boltzmann's real interest zone: the search for a demonstration of Clausius' second law for cyclic processes. The immense Boltzmann's scientific production remains one of the most important from the modern age until now. Among the numerous and distinguished hermeneutical works on Boltzmann, we have focused on a particular one: Planck's genial use of Boltzmann's kinetic model that lead to the equation $S = k \log W$
.

As for Gibbs, we have sketched out the foundations of his thermodynamic theory and the conceptual path through which he delivered a geometrical formulation of Clausius' Second Law. And secondly, we have tracked back the origin of his statistical formulation that maintains an analogical relation with the fundamental laws of thermodynamics, in the specific case of reversibility.

In the discussion we have compared Gibbs' statistical entropy and Shannon's function. We have underlined the differences between them: both on the formal level and the ontological one.

We would like to conclude with some general reflections on the importance of the historical method that constitutes the methodological dorsal of our researches. Dealing with entropy (and the Second Law) remains a challenging issue.[36] Entropy's semantic and epistemological plurality stands as the main source of ambiguities. On top of that, in a certain measure the richness emerging from a plurality of complementary approaches can translate into misconceptions. Strictly referring to original papers very often allows disambiguating cognitive knots as it has been the case of Gibbs versus Shannon entropies, as we have discussed in this paper. Nevertheless, it is worth noticing that the majority of scientific papers and textbooks prefer not to follow a historical approach as Kuhn critically outlines:

> Textbooks, however, being pedagogic vehicles for the perpetuation of normal science, have to be rewritten in whole or in part whenever the language, problem–structure, or standards of normal science change. In short, they have to be rewritten in the aftermath of each scientific revolution, and, once rewritten, they inevitably disguise not only the role but the very existence of the revolutions that produced them. […] Textbooks thus begin by truncating the scientist's sense of his discipline's history and then proceed to supply a substitute for what they have eliminated. Characteristically, textbooks of science contain just a bit of history, either in an introductory chapter or, more often, in scattered references to the great heroes of an earlier age. From such references both students and professionals come to feel like participants in a long–standing historical tradition. Yet the textbook–derived tradition in which scientists come to sense their participation is one that, in fact, never existed. (Kuhn 1962, pp. 137-138)

We conclude with an example. An example of misconception that can be framed among the cases of a lack of historical method. It is the case of the famous Clausius' *motto* briefly

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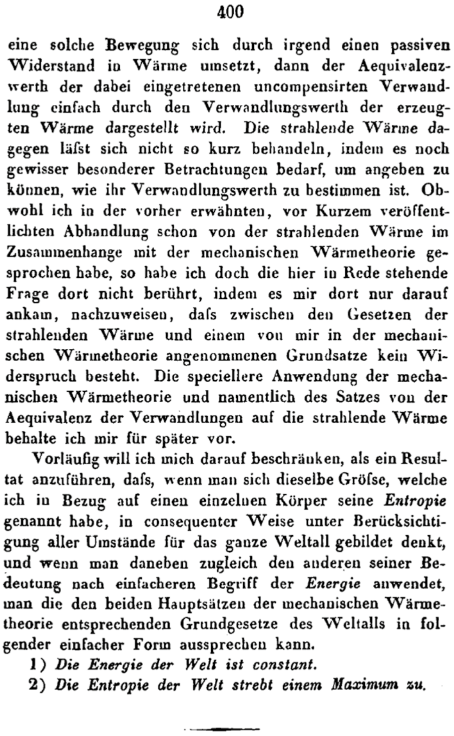
[36] In the history of science, we have significant examples of textbooks written by scholars, researchers during their teachings job (Mellone and Pisano, 2012; Pisano, 2007a, 2007b, 2009a, 2009b, 2011a, b, 2013a, b, 2015, 2016). One can consider the new born theories of heat and thermodynamics and related textbooks used at the end of the 19th century: Jean Baptiste JosephFourier's (1768–1830) *Théorie analytique de la chaleur* (Fourier 1822) and the positivist Gabriel Lamé's (1795–1870) *Leçons sur la théorie analytique de la chaleur* (Lamé1836,1861a,b) focusing the physical–mathematical relationship (Pisano 2013a,b); in the theory of heat and without considering experimental aspects of the scientific process of knowledge. For example, between *chaleur* and *calorique* and the second principle are avoided. Therefore, Reech's *théorie général des effets dynamiques de la chaleur* (Reech 1853, 1854) in which he adopted and generalized Sadi Carnot's (1796–1832)and Clapeyron's (1799–1864)reasoning in order to obtain a general formula from which each of the two theories (on caloric and on heat) can be derived under the right conditions (Pisano, 2001, 2010). An Italian scholar Paolo Ballada (1815–1888) called Paul de Saint–Robert published (at the time into French language and translated in various languagesnot in Italian) a textbooks, *Principes de thermodynamique.* (Saint-Robert 1865, 1870a,b,c) whichfor the first timepresented a historical part concerning the first biographical notes on Sadi Carnot. In this textbook, the second principle is very much emphasized. Just to mention other: Zeuner, Verdet, Hirn, Combes, Clausius, Jacquier, Jamin (Gillispie and Pisano 2014, Table 10.2, pp. 326–327).

stating the First and Second Laws of Thermodynamics (Fig. 8). The most of papers and textbooks—on this matter—simply report:

1. The energy of the universe is constant
2. The entropy of the universe tends to maximum

hence omitting the premise introducing them. A premise that is crucial since it actually stands as the logical requisite of a *hypothetical syllogism* whose conclusion translates into two truly universal laws concerning the variation of energy and entropy. The apodictic of such syllogism strictly depends on the truth of the hypothesis, that is to say on the possibility to extend to "the entire universe—consistently and with regards to all circumstances" the concepts of entropy and energy as well as the laws obtained for a single system. In this framework, the universal laws formulated in such impressive way does not stand as absolute, but their validity is relative to the validity of the hypothesis.



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eine solche Bewegung sich durch irgend einen passiven Widerstand in Wärme umsetzt, dann der Aequivalenzwerth der dabei eingetretenen uncompensirten Verwandlung einfach durch den Verwandlungswerth der erzeugten Wärme dargestellt wird. Die strahlende Wärme dagegen läſst sich nicht so kurz behandeln, indem es noch gewisser besonderer Betrachtungen bedarf, um angeben zu können, wie ihr Verwandlungswerth zu bestimmen ist. Obwohl ich in der vorher erwähnten, vor Kurzem veröffentlichten Abhandlung schon von der strahlenden Wärme im Zusammenhange mit der mechanischen Wärmetheorie gesprochen habe, so habe ich doch die hier in Rede stehende Frage dort nicht berührt, indem es mir dort nur darauf ankam, nachzuweisen, daſs zwischen den Gesetzen der strahlenden Wärme und einem von mir in der mechanischen Wärmetheorie angenommenen Grundsatze kein Widerspruch besteht. Die speciellere Anwendung der mechanischen Wärmetheorie und namentlich des Satzes von der Aequivalenz der Verwandlungen auf die strahlende Wärme behalte ich mir für später vor.

Vorläufig will ich mich darauf beschränken, als ein Resultat anzuführen, daſs, wenn man sich dieselbe Gröſse, welche ich in Bezug auf einen einzelnen Körper seine *Entropie* genannt habe, in consequenter Weise unter Berücksichtigung aller Umstände für das ganze Weltall gebildet denkt, und wenn man daneben zugleich den anderen seiner Bedeutung nach einfacheren Begriff der *Energie* anwendet, man die den beiden Hauptsätzen der mechanischen Wärmetheorie entsprechenden Grundgesetze des Weltalls in folgender einfacher Form aussprechen kann.

1) *Die Energie der Welt ist constant.*
2) *Die Entropie der Welt strebt einem Maximum zu.*

Now I will limit myself to state one result. If for the entire universe – consistently and with regards to all circumstances – we imagine to determine the same quantity that, for a single system, I have called entropy and if, at the same time, we introduce the fundamental concept of energy, then both theorems of the mechanical theory of heat can be stated as fundamental laws of the universe in the following simple manner.

1) The energy of the universe is constant
2) The entropy of the universe tends to a maximum

Fig. 8 Clausius' First and Second Law for adiabatically isolated systems as conclusion of 1865 paper. (Clausius 1865, p. 400; Authors' translation). Source: http://www.archive.org (public domain)

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