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The Origins of the Entropy Concept

Olivier DARRIGOL
CNRS : Rehseis
83, rue Broca
75013 Paris

To this day entropy remains a strange, difficult, and multiform concept. Even the great Henri Poincaré renounced precisely defining energy and entropy. In order to justify the success of the two laws of thermodynamics for his students at the Sorbonne, he turned to history:

> Pour expliquer par quelles raisons tous les physiciens ont été amenés à adopter ces deux principes [la conservation de l'énergie et la croissance de l'entropie], je n'ai rien trouvé de mieux que de suivre dans mon exposition la marche historique. Le spectacle des longs tâtonnements par lesquels l'homme arrive à la vérité est d'ailleurs très instructif par lui-même. On remarquera le rôle important joué par diverses idées théoriques ou même métaphysiques, aujourd'hui abandonnées ou regardées comme douteuses. Service singulier que nous a ainsi rendu ce qui est peut-être l'erreur! Les deux principes, appuyés sur de solides expériences, ont survécu à ces fragiles hypothèses, sans lesquelles ils n'auraient peut-être pas encore été découverts. C'est ainsi que l'on débarrasse la voûte de ses cintres quand elle est complètement bâtie.

Following Poincaré's advice, I will show you the scaffolding and seek in the past some clues on the necessity of the entropy concept and on the tensions between its various meanings.[1]

As is well known, there are at least two basic meanings of entropy, one belonging to macroscopic thermodynamics, the other to statistical mechanics. The first derived from studies of the performance of the steam engine, the second from the Maxwell-Boltzmann kinetic theory of gases. I will follow this natural order, beginning with Sadi Carnot's innovative approach to the theory of the steam engine.

1 Classical entropy

Carnot's theorem

In his *Traité sur la puissance motrice du feu* of 1824, Sadi Carnot relied on an analogy with hydraulic machines, imitating the forms of reasoning that his father Lazare had introduced in the latter domain. His first fundamental remark was that the production of work by thermal means depended on a temperature difference that permitted "the fall of caloric." The analogy with hydraulic engines then suggested that in an optimal heat engine there should be no temperature change without a corresponding change of volume of the working substance. Carnot described the simplest cyclic process that meets this criterion, which we now call a Carnot cycle.[2]

Then came Carnot's important theorem: a reversible engine has the highest possible efficiency among all engines that work between two given temperature sources. The proof is based on two axioms: the conservation of the caloric, and the impossibility of a certain form of perpetual motion. Suppose, Carnot reasoned *ab absurdo*, that there exists an engine that is more efficient than the reversible engine. Then the work produced by the hypothetical engine would be superior to the work needed to return the "fallen" caloric to its original level by operating the reversible engine

[1] Henri Poincaré, Thermodynamique, Sorbonne lectures of 1888–89 ed. by J. Blondin (Paris, 1892), XIII–XIV.
[2] Sadi Carnot, *Réflexions sur la puissance motrice du feu* (Paris, 1824). Cf. Truesdell 1980.

backwards. The simultaneous operation of the two engines would then permit the indefinite production of work without any compensation. In order to avoid this consequence, Carnot's theorem must hold.

As a corollary to this theorem, all reversible bithermal engines must have the same efficiency: the ratio of the produced work to the transferred heat is a function solely of the temperatures of the source and sink. Carnot used this wonderful property to derive what we now call Carnot-Clapeyron relations,[3] that is, relations between the constitutive properties of fluids and the universal efficiency function. Although most of Carnot's results did not survive the later rejection of caloric, his theorem and the style of its derivation and application had a brilliant future. Ideal machines and processes, reversible cycles, *ab absurdo* reasoning, and organizing principles are the gist of modern thermodynamics.

In 1845, William Thomson became aware of Carnot's long-neglected treatise through Emile Clapeyron's derivative memoir of 1834. The young natural philosopher quickly understood the predictive power of Carnot's theory and developed it in a series of publications. At the same time, he admired James Joule's contemporary experiments, which seemed to contradict the conservation of caloric on which Carnot's theorem was based. To face this dilemma, he tentatively assumed that heat could be created but never annihilated by mechanical means. This compromise saved the demonstration of Carnot's theorem, but led to a further paradox:[4]

> When "thermal agency" [a temperature difference]... is spent in conducting heat through a solid, what becomes of the mechanical effect which it might produce? Nothing can be lost in the operations of nature, no energy can be destroyed... It might appear that the difficulty would be entirely avoided by abandoning Carnot's fundamental axiom [the conservation of heat during its "fall"]; a view which is strongly urged by Mr. Joule... If we do so, however, we meet with innumerable other difficulties, insuperable without farther experimental investigation, and an entire reconstruction of the theory of heat from its foundation. It is in reality to experiment that we must look; either for a verification of Carnot's axiom, and an explanation of the difficulty we have been considering; or for an entirely new basis of the Theory of Heat.

Clausius's new thermodynamics

With this empiricist attitude Thomson vainly scrutinized contemporary steam measurements. The true key to the paradox was a modification of Carnot's theoretical reasoning, as Rudolf Clausius explained in his fundamental memoir of 1850 on the motive force of heat. Then a simple *Privatdozent* at the University of Berlin, Clausius remarked that one could simultaneously assume, in a Carnot engine, the transfer of heat from the hot source to the cold source and the transformation of part of this heat into work. Carnot's theorem could then be maintained without contradicting Joule's statement of the equivalence between heat and work. But the theorem could no longer be based on the impossibility of perpetual motion. Imitating Carnot's *ab absurdo* reasoning, Clausius supposed the existence of a bithermal engine with a higher efficiency than a reversible engine. The work produced by the hypothetical engine could be used to run a reversed Carnot engine between the same sources. The net result would be a transfer of heat from a cold source to a hot source without any compensation. The impossibility of such a transfer implies Carnot's theorem.[5]

As this impossibility agreed with "the known behavior of heat," Clausius made Carnot's theorem his second principle. His first principle was a statement of Joule's equivalence between heat and work: "In all cases when work is produced by heat, a quantity of heat is consumed that is proportional to this work, and reciprocally the same quantity of heat can be produced by

[3]The prototype is the relation $\frac{\partial P}{\partial \theta}|_V = \mu l$ where P is the pressure of the fluid, θ its temperature, V its volume, and l its latent heat of expansion, and $\mu(\theta)d\theta$ is the universal efficiency ratio for a temperature fall $d\theta$.

[4]William Thomson, "An account of Carnot's theory of the motive power of heat, with numerical results deduced from Regnault's experiments on steam," Royal Society of Edinburgh, *Transactions*, 16 (1849), 541–574, also in *Mathematical and physical papers*, 6 vols. (Cambridge, 1882–1911), on 118n–119n.

[5]Rudolph Clausius, "Über die Bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen," *Annalen der Physik und der Chemie*, 79 (1850), 368–397, 500–524. Cf. Daub 1971.

consuming an equal amount of work."[6]

As we may retrospectively judge, Clausius's memoir provided a complete and secure foundation for thermodynamics. Clausius nonetheless sought a deeper understanding of the principles. In particular, he tried to compensate for the loss of intuitive understanding implied by the demise of the caloric. In Carnot's original reasoning the work produced by a steam engine corresponded to the "fall of the caloric," that is, to its transfer from a state of higher to lower potential energy. What happens to this idea when heat is no longer conserved?

Clausius's transformation value

Clausius answer to this question appeared in a memoir of 1854 entitled "On a modified form of the second principle of the mechanical theory of heat." This is one of the strangest memoirs in the entire history of physics, owing to the odd mixture of the new thermodynamics with older ideas reminiscent of Carnot's theory. In 1850, Clausius had maintained a connection with Carnot's theory by considering that in a cycle of a bithermal machine two simultaneous transformations occurred: a transfer of heat (without loss) from the hot source to the cold source, and a conversion of part of the heat released by the hot source into work. In analogy with Carnot's relation between the fall of heat and the production of work, Clausius declared that for a reversible machine the first transformation was "equivalent" to the second. He further assumed that the equivalence rested on the equality of the "equivalence values" (*Equivalenzwerthe*) of the two transformations, just as in a hydraulic machine the decrease in the potential energy of the water must be equal to the work produced by the machine.[7]

In general for any number of thermal sources and for a given amount of mechanical work produced, Clausius regarded the evolution of the sources as resulting from a combination of two kinds of transformations: heat transfer from one source to another, conversion of heat from one source into work (of course, this decomposition is not unique when there is more than one source). He assumed that the equivalence-value of the product of two transformations was equal to the product of their equivalence-values, and that the equivalence-value of any transformation that could be realized through a reversible cycle of a thermodynamic machine was equal to zero. Noting $Q_{\theta_2}^{\theta_1}$ a transformation of the first kind, and Q_θ a transformation of the second kind, these axioms imply

$$w(Q_\theta) = Qf(\theta), \qquad w(Q_{\theta_2}^{\theta_1}) = Q\,[f(\theta_1) - f(\theta_2)] \tag{1}$$

for the equivalence-values w, wherein f is a universal function of the temperature.

Clausius next considered a transformation operated through a bithermal machine taking the heat Q_1 from the source at temperature θ_1 and yielding the heat $-Q_2$ to the source at temperature θ_2. This transformation may be regarded as the combination of the conversion of the heat $Q_1 + Q_2$ from the hot source into work, and the transfer of the heat $-Q_2$ from the hot source to the cold source. If the bithermal machine has performed a reversible cycle, the two axioms lead to

$$(Q_1 + Q_2)f(\theta_1) + (-Q_2)\,[f(\theta_1) - f(\theta_2)] = 0\ , \tag{2}$$

$$\text{or} \qquad Q_1 f(\theta_1) + Q_2 f(\theta_2) = 0\ . \tag{3}$$

As Clausius knew, Thomson had defined the absolute temperature T so that in a Carnot cycle the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{4}$$

holds. With this definition, $f(\theta)$ must be proportional to $1/T$. Clausius generalized these considerations to an arbitrary number of sources to get the expression

$$w = \oint \frac{\delta Q}{T} \tag{5}$$

[6] Clausius, ref. 5, also in *The mechanical theory of heat, with its applications to the steam-engine and to the physical properties of bodies* (London, 1867), on 18.

[7] Clausius, "Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie," *Annalen der Physik und der Chemie*, 93 (1854), 481–506.

of the value of a combination of infinitesimal transformations in which the net heat δQ is released by the source at temperature T. For a transformation that can be realized through a reversible cycle of a thermodynamic machine, the condition

$$\oint \frac{\delta Q}{T} = 0 \tag{6}$$

must hold. Clausius further deduced the inequality

$$\oint \frac{\delta Q}{T} < 0 \tag{7}$$

for a transformation that can be realized through an irreversible cycle of a thermodynamic machine. If the opposite inequality held, the integral could be divided into a vanishing part and a part for which all the δQ's are positive so that work could be produced from heat without compensatory heat fall.

Clausius's entropy

It should be emphasized that Clausius's "transformation value," unlike his later "entropy," concerned the transformations of an environment described as a system of heat sources and a work recipient. Its primary purpose was to analytically express the fact that such a transformation can or cannot be realized through a reversible cycle of a thermodynamic machine. However, toward the end of his memoir Clausius shifted the focus from the environment to the working substance of a machine operating in this environment. For a reversible, quasi-static cycle of the substance, he argued, its successive temperatures are identical with the temperatures of the sources with which it exchanges heat. The transformation value $\oint \delta Q/T$ thus becomes a property of the substance. Since it vanishes for any cycle, $\delta Q/T$ must be an exact differential.

In 1854 Clausius used this remarkable property to ease the derivation of relations of the Carnot-Clapeyron type. Much later, in 1865, he forged the word "entropy" from the Greek $\tau\rho o\pi\grave{\eta}$ (transformation), to denote the integral of this differential from a fixed reference state. He also considered irreversible transitions of the substance from one state of equilibrium to another. After such a transition the substance can be returned to its original state through a reversible transformation. During the resultant cycle, the inequality $\delta Q/T < 0$ must hold. Consequently, the entropy of the global system that includes the substance and all the sources can only increase; while its energy is of course invariable. Clausius concluded with two cosmic laws:[8]
"The energy of the world is constant."
"The entropy of the world tends to a maximum."

Reception

The beautiful symmetry of this statement, and the mathematical advantages of explicitly introducing the integral of the complete differential $\delta Q/T$ did not suffice to impose the entropy concept in early thermodynamics. Clausius himself preferred the now forgotten concept of disgregation,[9] which he intuitively grasped as the dispersion of the molecules of a body. In Britain, the engineer William John Macquorn Rankine had introduced the integral $\int \delta Q/T$ in 1853, and in 1854 Thomson had given $\sum_i Q_i/T_i = 0$ as "the mathematical expression of the second principle" for a reversible cycle of a system exchanging the heats Q_i with a series of sources at the temperatures T_i.[10] Yet the leaders of British thermodynamics judged the entropy concept too abstract and rather reasoned in terms of available and dissipated energy, which directly referred to the human ability to exploit energy sources—and, for Thomson, to God's unwillingness to intervene in the created world. In their treatises on heat James Clerk Maxwell and his friend Peter Guthrie Tait cared so little about Clausius's entropy as to give an erroneous definition of it.[11]

[8] Clausius, "Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie," *Annalen der Physik und der Chemie*, 125 (1865), 353–400, also in *Mechanical theory of heat*, ref.6, on 365.

[9] The disgregation Ξ is defined by $-Td\Xi = -d\Omega + \delta W$, where Ω is the (average) potential of the internal forces of the system and δW the work of external forces. If Y denotes the "heat content" $U - \Omega$, the disgregation is related to the entropy by $dS = dY/T + d\Xi$. As remarked in Klein 1969, statistical mechanics leads to a similar decomposition if only the Halmiltonian has two separate, kinetic and potential terms.

[10] Cf. Truesdell 1980.

[11] Cf. Smith and Wise 1989.

French, German, and American thermodynamicists were more receptive to this notion. In the 1870s, the engineer François Massieu discovered that the entropy function could be used to form thermodynamic potentials from which all thermodynamic properties of a substance resulted by simple derivations; and the American Josiah Willard Gibbs founded the laws of chemical equilibrium on Clausius's entropy law. In the 1880s, Hermann von Helmholtz recovered similar laws thanks to the "free energy" $U - TS$, and his disciple Max Planck reformulated thermodynamics on the basis of the energy and entropy laws. By the end of the century, the entropy concept belonged to the standard equipment of well-educated physicists, although some of them still deplored the abstract character of this concept and rather reasoned in terms of the free energy.[12]

2 Statistical entropy

A high level of abstraction was the price to be paid for a powerful thermodynamics based on macroscopic principles only. The founders of thermodynamics, especially Rankine, Clausius, and Maxwell, sought a more intuitive understanding of this science in kinetic-molecular theories that they developed in parallel to the phenomenological approach. In two memoirs of 1860 and 1867 Maxwell developed the statistical description of a gas in terms of the velocity distribution and the relative frequency of various kinds of molecular encounters.[13]

Maxwell's demon

Famously, Maxwell used the kinetic-molecular picture to "pick a hole" in the second law of thermodynamics. In a letter to Tait of December 1867, he argued that a "finite being" who could "see the individual molecules" would be able create a heat flow from a cold to a warm body without expense of work. The being only had to control a diaphragm on the wall between warm and cold gas, and let solely the swiftest molecules of the cold gas pass into the warm gas. In discussions with William Thomson and William Strutt, Maxwell related this exception to the second law of thermodynamics with another obtained by mentally reversing all molecular velocities at a given instant. "The 2nd law of thermodynamics," he wrote in 1870, "has the same degree of truth as the statement that if you throw a tumblerful of water into the sea you cannot get the same tumblerful of water out again." In 1878, he further remarked (probably inspired by Gibbs' paradox) that the dissipation of work (or the mixing entropy in Gibbs' terms) during the interdiffusion of two gases depended on our ability to separate them physically or chemically, and concluded: "The dissipation of energy depends on the extent of our knowledge.... It is only to a being in the intermediate stage, who can lay hold of some forms of energy while others elude his grasp that energy appears to be passing inevitably form the available to the dissipated state."[14]

Boltzmann's first entropy formulas

Maxwell's remarks, insightful as they were, remained purely qualitative and did not directly relate entropy and probability. Roughly speaking, the British disliked entropy too much, and the Germans disliked molecular-probabilistic theories too much to seek such a relation. The Austrian physicist Ludwig Boltzmann had neither of these aversions. In 1866, assuming a periodic motion of the atoms of the system and evoking natural definitions of the heat and work exchanged during slow deformations of the system, he gave a first mechanical interpretation of the entropy concept:

$$S = \sum_i 2 \ln (\tau \bar{T}_i) \ , \tag{8}$$

where τ is the period of the motion and $\bar{T}_i$ the average kinetic energy of the atom i. He thus launched a German trend to produce direct analogies between thermodynamic systems and special (periodic

[12] Cf. Klein 1972.

[13] James Clerk Maxwell, "Illustrations of the dynamical theory of gases," *Philosophical magazine*, 19 (1860), 19–32; 20 (1860), 21–37; "On the dynamical theory of gases," Royal Society of London, *Philosophical transactions*, 157 (1867), 49–88. Cf. Brush (and Everitt) 1973.

[14] Maxwell to Tait, 11 Dec. 1867, in P. Harman, ed., *The scientific letters and papers of James Clerk Maxwell*, vol. 2 (Cambridge, 1995), 328-334; Maxwell, *Theory of heat* (London, 1871), 328–329; Maxwell to Strutt, 6 Dec. 1870, *Letters and papers*, vol. 2, 582–583; Maxwell, "Concerning demons," undated note to Tait, in C.G. Knott, *Life and scientific work of Peter Guthrie Tait* (Cambridge, 1911) 214–215; Maxwell, "Diffusion," *Encyclopedia Britannica* (1878), also in *Scientific papers*, vol. 2, 625–646, on 646. Cf. Klein 1970b.

or monocyclic) mechanical systems without probabilistic considerations and ignoring irreversible processes. I skip these developments, because they have left few traces in modern physics save for the theory of adiabatic invariants in mechanics.[15]

In most of his later writings on kinetic-molecular theory, Boltzmann developed the statistical point of view found in Maxwell's kinetic theory of gases of 1867. For the number of collisions between two gas molecules occurring within the time interval δt, with initial velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ (within ranges d^3v_1 and d^3v_2), with a relative impact parameter comprised between b and $b+db$, and with a relative azimuthal angle comprised between ϕ and $\phi+d\phi$, Maxwell gave the natural expression

$$dN = |\mathbf{v}_1 - \mathbf{v}_2|\ \delta t\ b\ db\ d\phi\ f(\mathbf{v}_1)\ d^3v_1\ f(\mathbf{v}_2)\ d^3v_2\ , \tag{9}$$

where $f(\mathbf{v})d^3v$ is the number of molecules per unit volume within the element d^3v around $\mathbf{v}$. He then applied this expression to a derivation of the equilibrium distribution of velocities (Maxwell's law) and to the computation of transport phenomena.[16]

In 1868, at the end of a series of generalizations of Maxwell's law, Boltzmann introduced the distribution $\rho(q_1, q_2, \cdots q_N\ ;\ p_1, p_2, \cdots p_N)\ d^Nq\ d^Np$ that gives the fraction of time spent by the system in the volume element $d^Nq\ d^Np$ of phase-space after a very long time has elapsed. Assuming that the trajectory of the system in phase-space filled the energy shell, he then proved that ρ was uniform over the energy shell. In modern terms, he assumed ergodicity and derived the micro-canonical distribution.[17]

Three years later, Boltzmann showed that any small subsystem of the original system was distributed according to the canonical law

$$\rho = \frac{1}{Z} e^{-\beta H}\ , \tag{10}$$

wherein H is the hamiltonian of the subsystem, β is a constant parameter to be identified to the inverse of temperature, and Z is a normalizing factor. He then submitted a canonically distributed system to an infinitesimal change of external conditions (corresponding for instance to a macroscopic change of temperature and volume). Identifying the work provided to the system during this change with the canonical average $< dH >$ of the resulting change of the hamiltonian, and the internal energy with the canonical average $< H >$ of the energy, he obtained the expression

$$\delta Q = d < H > - < dH > \tag{11}$$

of the exchanged heat. The product $\beta\delta Q$ is then easily seen to be the differential of $\beta < H > + \ln Z$. In other words, there exists an entropy function, which Boltzmann soon rewrote as[18]

$$S = -\int \rho\ \ln \rho\ d^Np\ d^Nq\ . \tag{12}$$

This is the first occurrence of a mathematical relation between entropy and probability. Remember that in this case Boltzmann defined the probability ρ as the fraction of time spent by the system around a given point of phase space after a very long time has elapsed. Remember also that his derivation of the expression of this probability depended on the assumption of ergodicity.

The H-theorem

As Boltzmann doubted the truth of this hypothesis, he simultaneously developed another approach to kinetic equilibrium in which he generalized Maxwell's collision formula (9) to molecules of arbitrary complexity, and even to the thermal interaction of two ensembles. Maxwell, however,

[15] Ludwig Boltzmann, "Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie," Kaiserliche Academie der Wissenschaften zu Wien, mathematisch-naturwissenschaftliche Klasse, *Sitzungsberichte*, 53 (1866), 195–220. Cf. Klein 1972; Bierhalter 1993.

[16] Maxwell, "Dynamical theory of gases", ref. 13.

[17] Boltzmann, "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten," *Wien. Ber.*, 58 (1868), 517–560, also in *Abhandlungen*, vol. 1, 49–96. Cf. Klein 1973.

[18] Boltzmann, "Analytischer Beweis des zweiten Hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht der lebendigne Kraft," *Wien. Ber.*, 63 (1871) 712–732, also in *Abhandlungen*, vol. 1, 288-308.

had only proved that the Maxwell distribution of velocities was invariant under molecular collisions; he had no satisfactory proof for the uniqueness of the equilibrium distribution.[19]

In order to remedy this defect, Boltzmann examined the evolution of an arbitrary velocity distribution under Maxwell's assumption for the collision number, and thus obtained the equation

$$\frac{\partial}{\partial t} f(\mathbf{v}_1, t) = \int \left[f(\mathbf{v'}_1) f(\mathbf{v'}_2) - f(\mathbf{v}_1) f(\mathbf{v}_2) \right] |\mathbf{v}_1 - \mathbf{v}_2| \; b \; db \; d\phi \; d^3 v_2 \; , \tag{13}$$

in which the velocities $\mathbf{v'}_1$ and $\mathbf{v'}_2$ denote the final velocities corresponding to the initial velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ in a collision of the kind (b, ϕ). This equation, now called the Boltzmann equation, was published in 1872 under the banal title: "Further studies on the thermal equilibrium among gas molecules." The Maxwell distribution is clearly invariant through this equation. In order to show that any other distribution evolved toward Maxwell's equilibrium distribution, Boltzmann considered the quantity

$$H = \int f \ln f \; d^3 v \tag{14}$$

(originally noted E), probably by analogy with his earlier entropy formula (12). As a consequence of the Boltzmann equation, H is a strictly decreasing function of time, unless the distribution is Maxwell's. This is the so-called H-theorem. Boltzmann further noted that the value of $-H$ corresponding to Maxwell's distribution was identical to Clausius's entropy. For other distributions, he proposed to regard this quantity as an extension of the entropy concept to states out of equilibrium, since it was an ever increasing function of time.[20]

As can be inferred from earlier publications of his, Boltzmann was aware of exceptions to Maxwell's collision formula and therefore could not possibly believe that the Botzmann equation and the decrease of H applied to every possible microscopic configuration of the molecular system. He nevertheless formulated the H-theorem in absolute terms (H "must necessarily decrease"), presumably because his main purpose was to retrieve macroscopic thermodynamics, not to point to exceptions. In 1876 his Viennese colleague Joseph Loschmidt remarked that the reversibility of the laws of mechanics implied that to every H-decreasing evolution of the gas system corresponded a reverse evolution for which H increased.[21]

To this "extremely pertinent" paradox Boltzmann replied (in the more intuitive case of the spatial distribution of hard spheres): "One cannot prove that for every possible initial positions and velocities of the spheres, their distribution must become more uniform after a very long time; one can only prove that the number of initial states leading to a uniform state is infinitely larger than that of initial states leading to a non-uniform state after a given long time; in the latter case the distribution would again become uniform after an even longer time." Boltzmann's intuition, expressed in the modern terminology of micro- and macro-states, was that the number of microstates compatible with a uniform macrostate was enormously larger than that compatible with a non-uniform macrostate. Consequently, an evolution of the gas leading to increased uniformity was immensely more probable. "Out of the relative number of the various state-distributions," Boltzmann went on, "one could even calculate their probability, which perhaps would lead to an interesting method for the computation of the thermal equilibrium."[22]

The combinatorial entropy

This is precisely what Boltzmann managed to do a few months later. The probability Boltzmann had in mind was proportional to the number of microstates corresponding to a given macrostate. Such a number is ill-defined as long as the configuration of the molecules can vary

[19]Boltzmann, "Über das Wärmegleichgewicht zwischen mehratomigen Gasmolekülen," *Wien. Ber.*, 63 (1871), 397–418, also in *Abhanlungen*, vol. 1, 237–258.

[20]Boltzmann, "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen," *Wien. Ber.*, 66 (1872), 275–370, also in *Abhandlungen*, vol. 1, 216–402.

[21]Boltzmann, *Abhalungen*, vol. 1, 295 (probability needed), 297 (energy fluctuations), 96 (special initial states), 317 (quote), 344 (quote); Joseph Loschmidt, "Über den Zustand des Wärmegleichgewichtes eines Systemes von Körpern mit Rücksicht auf die Schwerekraft," *Wien. Ber.*, 73 (1876), 128–142.

[22]Boltzmann, "Bemerkungen über einige Probleme der mechanischen Wärmetheorie," *Wien. Ber.*, 75 (1877), 62–100, also in *Abhandlungen*, vol. 2, 112–148, on 117, 120, 121.

continuously. Boltzmann, who generally believed in a discrete foundation of analysis, began with a "fiction" wherein the energy of a molecule can only be an integral multiple of the finite element ϵ. Then a list of N integers giving the number of elements on each molecule defines the microstate of the gas, or "complexion." The macrostate according to Boltzmann is the discrete version of the energy distribution: it gives, for each possible value $i\epsilon$, of the energy, the number N_i of molecules with this energy. The probability of such a macrostate is proportional to its "permutability" $N!/N_1!N_2!\cdots N_i!\cdots$. For a given value of the total number $\sum_i N_i$ of molecules and of the total energy $\sum_i N_i i\epsilon$ and in the Stirling approximation of factorials, the permutability is a maximum when N_i is proportional to $e^{-\beta i\epsilon}$ (wherein β is the Lagrange multiplier associated to the constraint over the total energy). Boltzmann next replaced the uniform division of the energy axis with a uniform division of the velocity-space, and took the continuous limit of the distribution N_i. This procedure yields Maxwell's velocity distribution. For any distribution N_i, the logarithm of the permutability is $-\sum_i N_i \ln N_i$ in the Stirling approximation (up to a constant), or $-H$ in the continuous version. Hence the entropy $-H$ measures the combinatorial probability of the velocity distribution, as Boltzmann already suspected in his reply to Loschmidt. This is the relation that Max Planck later wrote as

$$S = k \ln W \ , \tag{15}$$

with W for Wahrscheinlichkeit (probability), and k for the so-called Boltzmann constant.[23]

In 1878, Boltzmann used the combinatorial probability to explain the existence of a mixing entropy for two chemically indifferent gases. In 1883, after reading Helmholtz's memoirs on the thermodynamics of chemical processes, he showed how his combinatorics explained the dependence of chemical equilibrium on the entropy of the reaction. In this context, Helmholtz (presumably drawing on Maxwell) distinguished between "ordered motion" that could be completely converted into work, and "disordered motion" that allowed only partial conversion. Accordingly, Boltzmann identified the permutability with a measure of the disorder of a distribution. The mixing entropy thus became the obvious counterpart of increased disorder.[24]

The H-curve

Boltzmann's probabilistic interpretation of the H function failed to silence criticism of the H-theorem. In 1894, British kinetic-theoreticians invited Boltzmann to the annual meeting of the British Association, in part to clarify the meaning of this theorem. One of them, Samuel Burbury, offered a terminological innovation: "molecular chaos," defined as the validity condition for Maxwell's collision formula. Intuitively, this assumption corresponds to the exclusion of specially arranged configurations, for instance those in which the velocities of closest neighboring molecules point toward each other. It should not be confused with Helmholtz's molar notion of disorder. As long as the gas remains molecularly disordered, the H function evolves according to the Boltzmann equation. Boltzmann did not entirely exclude ordered microstates. He even indicated that an initially disordered microstate could occasionally pass through ordered microstates leading to entropy-decreasing fluctuations, although he judged such events extremely improbable.[25]

To this view Boltzmann's British interlocutors opposed a refined version of the reversibility paradox. H-decreasing and H-increasing states of an isolated gas should be equally frequent, they reasoned, for they correspond to each other by time-reversal. In order to elucidate this point, Boltzmann discussed the shape of the real H-curve determined by molecular dynamics and its relation with the variations of H given by the Boltzmann equation. The real curve results from the cumulative effect of the rapid succession of collisions in the gas. It therefore has an extremely irregular shape, and does not admit a well-defined derivative in the ordinary sense. The refined

[23]Boltzmann, "Über die Beziehung zwischen dem zweiten Haupsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitzrechnung respektive den Sätzen über das Wärmegleichgewicht," *Wien. Ber.*, 76 (1877), 373–435, also in *Abhandlungen*, vol. 2, 164–223; M. Planck, "Über das Gesetz der Energieverteilung im Normalspektrum, *Annalen der Physik*, 4 (1901), 553–563. La "probabilité" de Planck n'est en fait qu'un nombre de complexions.

[24]Boltzmann, "Über die Beziehung der Diffusionsphänomene zum zweiten Hauptsatze der mechanischen Wärmetheorie," *Wien. Ber.*, 78 (1878), 733–763, also in *Abhandlungen*, vol. 2, 289–317; "Über das Arbeitsquantum, welches bei chemischen Verbindungen gewonnen werden kann," *Wien. Ber.*, 88 (1883), 861–896.

[25]See various articles by E.P. Culverwell, G.H. Bryan, and S.H. Burbury in *Nature*, 51 (1895); Boltzmann, "Nochmals das Maxwellsche Verteilungsgesetz der Geschwingigkeiten," *Annalen der Physik*, 55 (1895), 223–224; *Gastheorie*, vol. 1, 20–21. Cf. Brush 1973, 616–626.

paradox of reversibility fails, because it implicitly identifies the decrease of H with the negative sign of its derivative.[26]

Boltzmann then offered the following interpretation of the decrease of H: For an initial macrostate out of equilibrium and for a finite time of evolution, the number of compatible microstates for which H decreases is much higher than the number of compatible microstates for which H increases. This statement is perfectly time-symmetrical. Over a very long time, Boltzmann explained, H is for the most very close to zero, and the frequency of its fluctuations decreases very quickly with their intensity. Hence, any significant value of H is most likely to be very close to a summit of the H-curve. From that point H may increase for some time, but this time is likely to be very short and to be followed by a long-term decrease.[27]

The following year Max Planck's assistant Ernst Zermelo formulated another objection to the H-theorem based on Poincaré's recurrence theorem. According to this theorem, any mechanical system (governed by Hamilton's equations) evolving in a finite space with a finite number of degrees of freedom returns, after a sufficiently long time, as close to its initial configuration as one wishes (except for some singular motions). In Zermelo's and Planck's opinion, the theorem excluded any derivation of the entropy law from a mechanical, molecular model. Boltzmann replied, with obvious weariness, that his description of the H-curve was perfectly compatible with recurrences. There was not any conflict with the second law of thermodynamics, as long as the relevant times were far beyond human accessibility. Through a simple calculation he estimated the recurrence time of a macroscopic gas sample to have some 10^{10} digits when measured in a human scale.[28]

Reception

To summarize, Boltzmann proposed three different relations between entropy and probability:

- the relation $S = -\int \rho \ln \rho \, d^N p \, d^N q$ between the equilibrium entropy of a system and the canonical probability of its phases (understood as a temporal frequency),
- the relation $S = -H = -\int f \ln f \, d^3 v$ for the entropy of a gas out of equilibrium and the velocity distribution f, with generalizations to polyatomic molecules and even to ensembles (a whole system regarded as a giant molecule),
- the relation $S = k \ln W$ between the entropy of a gas out of equilibrium and the combinatorial probability W of its macrostate.

Boltzmann regarded the second relation as most important, because it included non-equilibrium states and because it could be established without the assumption of ergodicity, which he did not trust. In his view the third relation only was a "mathematical illustration" of the second, because the equiprobability of the relevant complexions ultimately depended on assumptions already made in earlier approaches, either ergodicity or generalized *Stosszahlansatz*. Thanks to the Boltzmann equation and the H-theorem, Boltzmann could prove the increase of the entropy defined by the second relation. But he clearly recognized that this derivation only had statistical validity, that improbable entropy-decreasing fluctuations could occur; and he provided insightful answers to the resulting paradoxes of reversibility and recurrence. As an epigraph to his lectures of 1898 on gas theory, he cited Gibbs' pronouncement: "The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability."[29]

British physicists, including Maxwell, welcomed Boltzmann's theory, which they regarded as a monumental, sometimes impenetrable but always deep extension of Maxwell's kinetic theory of gases. In America, the Yale mathematician Josiah Willard Gibbs developed Boltzmann's and Maxwell's ensemble approach in his supremely elegant, general, and powerful *Statistical mechanics*

[26]Boltzmann, "On certain questions of the theory of gases," *Nature* 51 (1895), 413–415, also in *Abhandlungen*, vol. 3, 535–544. Cf. P. and T. Ehrenfest 1909; Klein 1970a.

[27]Paul Ehrenfest later illustrated this behavior with an urns-and-balls model : cf. Klein 1970a.

[28]Poincaré, "Sur le problème des trois corps et les équations de la dynamique," *Acta mathematica*, 13 (1889), 1–270; E. Zermelo, "Über einen Satz der Dynamik und die mechanische Wärmetheorie," *Annalen der Physik*, 57 (1896), 485–494; Boltzman, "Entgegnung auf die Wärmetheoretischen Betrachtungen des Herrn E. Zermelo, ibid., 57 (1896), 773–784, also in *Abhandlungen*, vol. 3, 567–578; "Über die sogenannte H-Kurve," *Mathematische Annalen*, 50 (1898), 325–332, also in *Abhandlungen*, vol. 3, 629–637. Cf. Brush 1873, vol. 2, 627–639.

[29]Boltzmann, *Vorlesungen über die Gastheorie*, 2 vols. (Leipzig, 1896, 1898), vol. 2, 19.

of 1902. In contrast, the Germans and the French ignored Boltzmann's theory because they believed that the ordinary methods of thermodynamics to be self-sufficient. Some of them, including Max Planck and Henri Poincaré even declared the impossibility of a kinetic-molecular understanding of the entropy law. This hostile attitude began to change toward the end of the century owing to three circumstances: the development of ionic or electronic theories of electricity, the rise of a new experimental microphysics of electrons, x rays and radioactivity, and the growing interest in black-body radiation. Boltzmann's and Maxwell's methods soon won important successes in these new fields. J.J. Thomson applied kinetic theory to the recombination of x-ray generated ions. The same Thomson, Paul Drude and Hendrik Lorentz developed the electron-theory of metals. Planck surmounted his original distaste of Boltzmann's theory, and based his famous derivation of the black-body law of December 1900 on the formula $S = k \ln W$, which he was first to write in this form.[30]

This spread of Boltzmann's methods did not necessarily imply a better understanding of their foundations. When a young admirer of these methods, Albert Einstein, began to reflect on them in 1902, he complained that the implied probabilities were ill-defined. The following year, he published his own foundations of statistical thermodynamics, mostly recovering aspects of Boltzmann's theory of which he was not aware, but also innovating in one capital respect, the interpretation of fluctuations. Boltzmann, Gibbs, and Maxwell were aware of the statistical fluctuations of thermodynamic quantities, and even knew out to compute them in the ensemble approach. At the same time, they judged these fluctuations to be so extremely rare to be devoid of physical meaning. Most radically, Planck believed that some unknown feature of the microdynamics prevented fluctuations from occurring at all, and he maintained the absolute validity of the entropy law until very late (about 1914).[31]

On the contrary, Einstein focused on the fluctuations around equilibrium that were negligible for Boltzmann and non–existent for Planck. He interpreted the probability in the Boltzmann relation $S = k \ln W$ as the temporal frequency of the fluctuations of the system around equilibrium, and the constant k as the measure of its thermal stability. In 1905, his analysis of Brownian motion showed how fluctuations could become observable at a mesoscopic scale. Inverting Boltzmann's relation, he derived the density fluctuations of black–body radiation from its empirically known entropy and thus arrived at the light–quantum hypothesis in the same year 1905. Whereas Maxwell and Boltzmann meant to provide a mechanical foundation of thermodynamics, Einstein used statistical mechanics to question this foundation.[32]

Conclusions

In my short history of the entropy concept, I have focused on the early period in which the basic principles of thermodynamics and statistical mechanics were first established. I am aware that this period does not exhaust the variety of meanings of entropy. Yet from Clausius's pioneering considerations to Einstein's re-foundation this concept evolved beyond recognition, from a meaning bound to Carnot's concern with steam-engine efficiency to a meaning designed to explore the microworld. The scene changed from the factory to the world of atoms. The plot turned from absolute laws of the macroworld to statistical laws representing the average behavior of enormous numbers of atoms. The man who most contributed to this stupendous evolution of the entropy concept, Ludwig Boltzmann, found himself under fire. When at the turn of the century a few major physicists began to appreciate his methods, they modified them for their own purposes, thus creating a number of different statistical thermodynamics. The later convergence toward a more uniform statistical mechanics "à la Gibbs" was never complete, as may be appreciated from the variety of expositions found in modern textbooks. Reflection on the meaning of entropy goes on, as the forthcoming conference purposes to illustrate.

To which extent can this reflection draw on nineteenth-century sources? I suppose none of you will be tempted to resurrect the Carnot-Clausius concept of transformation, which dragged

[30] Cf. Klein 1972a; Darrigol 1992.
[31] Cf. Darrigol 1992.
[32] Cf. Klein 1967; Renn 1997.

along the antiquated concept of heat as a substance. Yet from this origin of entropy it is well worth remembering that the concept has to do with human ability to exploit the energy stored in a given system. This connotation prepares the statistical interpretation, for the inaccessibility of certain forms of energy depends on the impossibility of acting on individual molecules, as emphasized by Maxwell. It is also good to remember that classical thermodynamics provides a consistent framework for defining entropy without any reference to the molecular level or to probabilistic considerations.

Nineteenth-century sources are most inspiring when it comes to the statistical meanings of entropy. Boltzmann was aware of the connections between various meanings of that kind, and offered deep insights into their apparent conflict with the thermodynamic meaning, for instance in his discussion of the H-curve. Unfortunately, his writings are hard to penetrate. Maxwell himself complained: "By the study of Boltzmann I have become unable to understand him. He could not understand me on account of my shortness and his length was and is an equal stumbling block to me."[33] As a result of Boltzmann's style, many of his ideas have been periodically rediscovered or attributed to his followers. At the same time, he could not foresee every modern development of the entropy concept. I am sure he would be glad to attend the forthcoming conference.

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