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Boltzmann: The Genius of Disorder

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Abstract The tragedy and greatness of the contribution of Ludwig Boltzmann cannot be understood without taking into account for the relevant scientific developments that took place in the nineteenth century, one of the most eventful periods in the history of science. The kinetic theory opened a new theoretical perspective in understanding natural phenomena. The introduction of new categories of order and disorder changed radically the point of view of those physicists that accepted Boltzmann's thesis and led, at the same time, to strong opposition to the Viennese Scientist. In this article, we present the academic situation, scientific theories, and disputes involving the Boltzmann's theories. A short introduction on the birth of the atomistic theories opens the article, while a view on the evolution of the concept of temperature and the definition of its unit quantity closes it.

Keywords History of science · Ludwig Boltzmann · Temperature definition · Thermodynamics

1 Introduction—The Atomistic Theory

In his epic philosophical poem titled *De Rerum Natura*, the Roman poet and philosopher Titus Lucretius Carus (Fig. 1) frequently discusses with his friend Gaius Memmius about atoms, which he calls *rerum primordia*. Lucretius understands and explains that substances are made of void space and atoms that are infinite in

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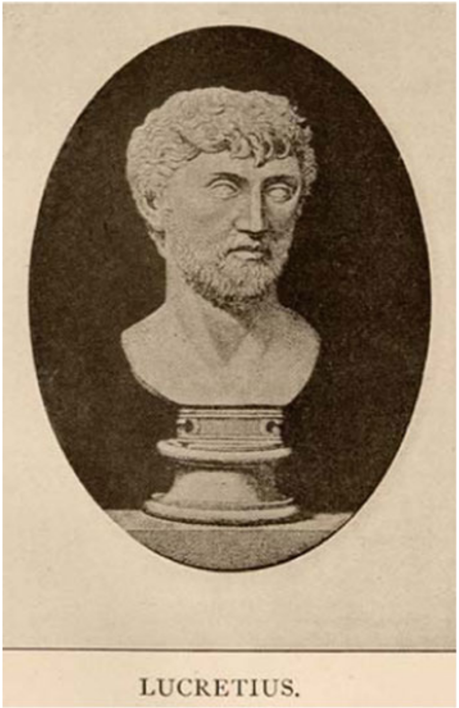

Fig. 1 Lucretius (98 BC–53 BC)

number. When matter decays, the atoms separate and “fly” away invisible, immutable, un-destroyable. He expresses the axiom that nothing can be produced from nothing, and that nothing can be reduced to nothing (*Nil fieri ex nihilo, in nihilum nil posse reverti*).

The shape of these corpuscules, their properties, their movements, the laws under which they enter into combination and assume forms and qualities appreciable by the senses occupy the first two books of the poem. This Epicurean view of Lucretius leads to a vitriolic polemic against superstition (Latin: “*religio*”), which is probably one of the reasons why the atomistic theories had to wait about 2000 years before being considered and accepted. The success of the atomistic theory is strongly based on the work of the great Austrian physicist Ludwig Boltzmann. He bridged the strong and well-established classical mechanics tradition of the nineteenth century with the extraordinary development of the quantum mechanics theory of the twentieth century.

2 Ludwig Boltzmann

Boltzmann (Fig. 2) was a great teacher; he had a surprising memory: he could teach for hours without reading a single word or equation. He was born to teach: his lessons were clear, witty, rich of anecdotes, sometimes even humorous. He frequently used innovative and unusual expressions such as “giantly small” and extended to a more philosophical view exotic concepts like multidimensional universes and curved

Fig. 2 Ludwig Boltzmann (1844–1906)

spaces. He was also a great pianist, showing a deep passion for Beethoven, and was a brilliant talker too. Nevertheless…

This great European physicist was born on 20th February 1844. This date represents an interesting coincidence. It's the so-called "Mardi Gras," the day that stays between the end of the carnival fun and the beginning of the serious Lenten season. All through his life, Ludwig Boltzmann continuously oscillated between those two extremes. Happy periods suddenly degenerated into sad times of deep mental depression. During one of those dark periods, he decided to tragically put the word "end" to his life. His general illness status, asthma, increasing blindness, together with the continuous aggressive opposition to his theories from the scientific academic communities, contributed to give the reason to his suicide. It was on 5th September 1906, in a beautiful hotel on the seaside in Duino along the south coast of the Austrian empire (now Italian territory). A terrible end with respect to the calm and beautiful land where he had decided to spend some nice holidays with his wife and daughter. A more dramatic sense is given by the fact that only one year before, the well-known Einstein "*annus mirabilis*" occurred. The four relevant articles by Einstein [1–4] contributed substantially to the foundation of modern physics and changed views on space, time, and matter. Substantially a confirmation of Boltzmann's view, but that in one year only it was still not accepted enough to give the required positive impact to his fragile mind.

3 Thermodynamics During the Nineteenth Century

The tragedy and greatness of the contribution of Ludwig Boltzmann cannot be understood without taking into account for the relevant scientific developments that took place in the nineteenth century, one of the most eventful periods in the history of science. Indeed, while the high degree of perfection attained by mechanics and astronomy had allowed the construction of a uniform interpretation of Nature, on the other side there was a multitude of phenomena such as heat, light, electricity, magnetism, and processes of life, which seemed to escape from this theoretical synthesis.

This was the reason why, throughout the 1800s, the investigation of mutual transformations of these phenomena and their reciprocal relations with mechanical processes acquired a fundamental importance. A decisive impetus to these studies came from the industrial revolution that began in those years, especially in England. And it was in England, in the mid-1800s, that the concept of energy found its full development. Next to matter, energy assumed the role of a fundamental quantity through which all natural phenomena could be addressed. It was the birth of a new science: thermodynamics. Also, thanks to previous observations from the German, Robert von Mayer (1814–1878) and from the French, Sadi Carnot, the English scientists William Thompson (1824–1907) (Lord Kelvin), and James Joule (1818–1889) established the foundations for this new scientific "building." Thermodynamics has therefore several fathers but few principles.

The first principle of thermodynamics states that energy, intended as the sum of mechanical work and heat, is a quantity that is conserved in any physical process. In the materialistic era, this seemed like a guarantee that nature is eternal and gave validity, once again, to the principle that nothing is created or destroyed, but everything changes. However, the same study of the steam engine, which had contributed decisively to the discovery of the first principle, had to reveal a pathological tendency of how things go in the world. Namely, that mechanical energy has a bad habit of constantly dissipating, becoming gradually unusable. This observation led Boltzmann to discover a major and general principle of all phenomena, a principle immediately promoted to the rank of the second law of thermodynamics. It indicates the flow of time's direction, which is that of the irreversible course of natural processes. Since in science, the best way to express concepts is by means of measurable quantities, a new abstract entity was introduced to represent this irreversibility: entropy, a quantity that increases (or rather, does not decrease) in every thermodynamic transformation. The formulation of the second principle put therefore an end to the chimera of the feasibility of a perpetual motion machine, producing energy at zero cost. This principle also led to the disconcerting conclusion that the universe—intended as a whole—is inevitably destined to a heat death or to the cessation of any transformation that was not pure heat transfer between all its particles.

Against this sort of death sentence for the universe and against the absolute irreversibility of physical processes, scientists had to again get help from mechanics and the ancient theory of atomism, this time, however, reformulated in a novel probabilistic variation. The serious difficulties that seemed to irremediably contrast the traditional conception of mechanical phenomena in the new science of thermodynamics have been resolved by a new line of research, statistical physics and, in particular, the kinetic theory of gases [5]. Already used in 1739 by Daniel Bernoulli in explaining gas pressure as a sum of the numerous collisions of molecules against the walls of the container, statistical physics had the greatest performers in the nineteenth century, being James Clerk Maxwell (1833–1879) and Ludwig Boltzmann.

The kinetic theory opened a new theoretical perspective in understanding natural phenomena: if heat was now interpreted as chaotic motion of molecules, the temperature and pressure of a body were nothing but mere phenomenological manifestations of the movement. Continuing the research of Maxwell, Boltzmann showed that whatever the initial distribution of velocities of the various gas molecules is, these collision velocities tend to be distributed according to a probabilistic universal law. During these studies, he introduced a function of speed that can never decrease and that is similar in every respect to entropy.

4 Measuring the Disorder

The concept of entropy could thus mean that large numbers of molecules tend to move from a lower probability state to another having a higher probability: the mysterious entropy, in Boltzmann's formulation, thereby became the measure of disorder in the motion of molecules. The relationship between the entropy of a body and its macroscopic state probability was expressed by the great Viennese physicist in terms of the universal constant of gases R. Max Plank replaced the R, expressed in units of energy, with the equivalent constant k, expressed in units of entropy, to formulate the famous formula $S = k \log W$, inscribed on Boltzmann's tombstone in the cemetery of Vienna. In this expression, S is the entropy, W is the probability, and k is the constant (called, in his honor, "Boltzmann constant"). As Plank wrote in his Nobel Prize lecture in 1920, "This constant is often referred to as Boltzmann's constant, although, to my knowledge, Boltzmann himself never introduced it [...] since he never gave thought to the possibility of carrying out an exact measurement of the constant." This measurement is now possible, thanks to modern and multiple techniques for determining it, and now the Boltzmann constant is the best candidate to replace the unit of temperature.

The increase in entropy of an irreversible phenomenon, which seemed to defy all traditional understanding of mechanics, was thus associated with a variation of the mechanical properties of a system of interacting particles. The introduction of these new categories of order and disorder radically changed the point of view of those physicists who accepted Boltzmann's thesis: under the light of statistical mechanics, it could now be acceptable that a mutual convertibility occurs between an ordered state (mathematically less probable) and a disordered one (or more probable). Thus, not the absolute but the probabilistic aspect of the second law of thermodynamics became more understandable. Statistical physics also led to a profound change in traditional views about the nature of physical knowledge: the macroscopic view of a physical phenomenon became separated, distinguished, and in some cases, even opposed to the microscopic view of the same phenomenon. The mechanical behavior of billions of molecules, which individually moved in the smallest portion of matter, could no more be treated individually but only statistically.

This opposition between the microscopic and macroscopic points of view also demonstrated that the steady-state visible of a body is actually the result of an invisible movement: it showed an innovative separation between experience and conceptual knowledge. This gave a discontinuity from the classical prejudice that fundamental laws of physics have to be strictly deterministic: this was a dangerous act and not yet an acceptable view by many. That was too much a revolutionary theory for several of those scientists who still strongly believed in a phenomenological and empirical knowledge of physical phenomena. Ernst Mach (1838–1916) and Wilhelm Ostwald (1853–1932) were the two among the stronger opponents to statistical and atomistic points of view. They officially condemned Boltzmann's theory in any public event and in their written documents.

According to Boltzmann, science should not be limited to a simple transcription of data. Letting him speak,

> No equation can exactly translate one event, such as it is. It idealizes and necessarily goes beyond experience.
>
> The fact that this necessarily results from our thought process itself, which is to add something to the experience and make a mental picture out of it. Phenomenology should not therefore claim to not exceed the experience but rather encourage us to do as much as possible.

The following development of science has shown all the flaws and uncertainties inherent in a program of physics based on purely phenomenological aspects. The discovery of discontinuous energy, the recognition of the electron mass, the development of increasingly refined models for the atom, the realization in the laboratory of fascinating phenomena such as the condensation of atoms at temperatures close to the absolute zero, only confirmed the validity of many of the positions for which Boltzmann had bravely fought, in extreme loneliness, against the official science of his time.

In 1897, Boltzmann had a dispute with Planck on the irreversibility of radiation phenomena which may have stimulated Planck's discovery of quantum mechanics in 1900. At this time, Planck thought that he could derive irreversible behavior for radiative processes without any assumptions on the initial states. Boltzmann could, however, show that this was not true and at the beginning of his second paper answering Planck, he made the following suggestion to Planck:

> It is certainly possible and would be gratifying to derive for radiation phenomena a theorem analogously to the entropy theorem from the general laws for these phenomena using the same principles as in gas theory. Thus, I would be pleased if the work of Dr. Planck on the scattering of electrical plane waves by very small resonators would become useful in this respect, which by the way are very simple calculations whose correctness I have never put in doubt. Only if Dr. Planck in his second communication claims again that no other process in nature is known, in which conservative forces lead to irreversible changes, I cannot agree.

Indeed Planck followed this recommendation and used Boltzmann's statistical methods for the derivation of his celebrated law for the blackbody radiation. Planck thereby used the additional assumption that classical oscillators absorb and emit energy only in integer multiples of the product of Planck's constant with the frequency of the radiation, which gave rise to the birth of quantum mechanics. In fact, in the framework of Boltzmann's statistical approach, it was quite common to introduce discrete energy levels to obtain a denumerable set of states. Boltzmann used this method already in his 1872 paper on the H-theorem. One may ask whether he considered this procedure only as a mathematical device or whether he attributed physical significance to it. In this connection, Ostwald reports that when he and Planck tried to convince Boltzmann of the superiority of purely thermodynamic methods over atomism at the Halle Conference in 1891, Boltzmann suddenly said

> I see no reason why energy shouldn't also be regarded as divided atomically.

5 Temperature

It's the same Boltzmann view of energy that now is the best candidate for a new definition of the kelvin. Temperature is the most "anthropic" quantity among the seven base units. The term comes from the Latin word "*temperare*" which has two similar and both significant meanings: it means the capability to control and regulate something and, in its more technical adoption, it refers to the beating of iron at the correct time for generating the required strength in the metal, before violently cooling it down. This was achieved by carefully experiencing the best "color" of the heated metal: the ancient and first example of optical thermometry! Temperature was introduced as a short-cut to measure other quantities and explain different phenomena. It described at the beginning only the sensations of warm and cold, and slowly became a required quantity when classical mechanics needed a unit to fit with observed and measurable laws, but in a time when the thermodynamics laws were still to come.

In a remote and unknown age, humans acquired a conscious use of the concepts of time, length, and mass. Almost at the same time or immediately after those concepts were formalized, some sort of standards were adopted. Units then started to be constantly improved in their definitions, to be adapted to the social and technical needs. The concept of temperature, in the form of heat, warm, or cold, was also a well-known concept throughout human evolution. But, unlike the other quantities, we had to wait until modern ages before having a unit defined for it. After Boltzmann's period and thanks to his work, we now know that in fundamental laws of physics, temperature appears as thermal energy, kT. We are now transferring this concept based on sensations, to the more significant principle having to do with energy, its transfer and its mean values.

There is no notice of an official meeting between Kelvin and Boltzmann (Fig. 3). We do not know if they ever met, but we do know that today their theories are coming together. After more than one century, their names can be found more and more on the same pages, giving the modern view for this quantity and giving to those two scientists their scientifically and historically due correlation.

Modern techniques for the determination of Boltzmann's constant are now acquiring sufficient accuracy to allow a definition of the unit of temperature, the kelvin, directly in terms of the constant itself [6–8]. This new definition, not a replacement of quantities, will have the advantage of being independent of any material substance, technique of realization, and temperature values or ranges. We have to consider that beside the

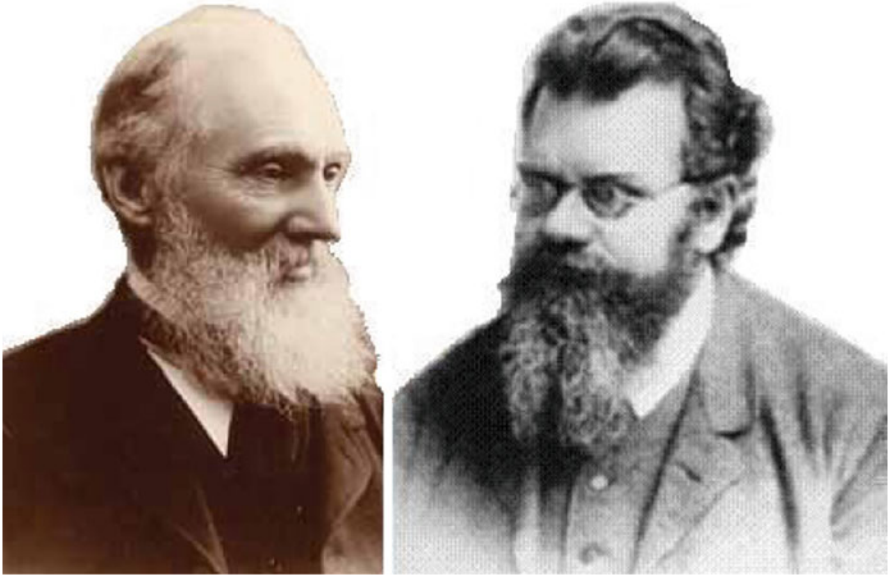

Fig. 3 William Thompson "Lord Kelvin" (1824–1907) and Ludwig Boltzmann. This picture was used as a logo for the IV International Workshop on Progress in Determining the Boltzmann Constant, Torino, Italy, September 2009

definition of the unit, the temperature scale, required for fast and highly reproducible measurements of this intensive quantity over wide ranges, is still mostly a practical scale. The International Temperature Scale (ITS) is well known to be only partially based on thermodynamic measurements such as at the fixed points or at its lower and upper ranges. It is used to transfer the definition of the unit from the temperature of the triple point of water to any upper or lower temperature value. But the present definition of the kelvin only refers to a thermodynamic state, without linking it to an energetic state or value. The more scientific instruments and techniques are improving measurement capabilities, the more the differences between the temperature measured using the ITS and the thermodynamic temperatures became evident. The new definition will therefore give significant improvements in terms of thermodynamic consistency to temperature measurements. Science will get the advantage of having the possibility to directly measure thermodynamic temperatures, while "every day" users will still have an ITS for practical purposes.

The deep physical meaning of temperature can now be expressed as a link between the anthropic concept of warm and cold and the physics of nature and energy. The Boltzmann work allowed the harmonization of the physical explanations of nature with the human experience of it.

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