

# A tribute to Boltzmann

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The name of Ludwig Boltzmann is at the heart of modern science. The constant carrying his name,  $k_B$ , is as old as quantum physics. It was introduced by Max Planck in the epochmaking paper read, on 14 December 1900, before the *German Physical Society*, in Berlin, and called after him, following Boltzmann's death [1]. Boltzmann embodied at once brilliant physics, an acute sense of humour, and pure human tragedy.

Boltzmann was born in 1844. In 1863 he enrolled as a student of physics in the Faculty of Science of Vienna. Under Josef Stefan he passed the MSc, the PhD and the 'Habilitation', the latter early in 1868. The swiftness may indeed surprise. It should be realized, however, that, before 1872, no dissertations had to be submitted for degrees in academic Austria. So he could be nominated in 1869 as professor of mathematical physics at the Karl-Franzens University of Graz. In his new position, he set out for a trip to Hermann von Helmholtz, in Berlin. In Helmholtz' laboratory the implications and consequences of Maxwell's brand new electrodynamics were being considered in detail. One of these, the relation between the dielectric constant,  $\epsilon$ , the diamagnetic constant,  $p$ , and the refraction index,  $n$ , proved crucial. Initially, the idea was that of Maxwell,  $n$  being considered as the geometrical mean of  $\epsilon$  and  $p$ , hence  $n = \sqrt{\epsilon p}$ . For insulators such as sulphur (colophonia, paraffin wax, ...)  $p$  would be equal to that of air, that is unity. So Maxwell's formula (1865) reduced to  $n = \sqrt{\epsilon}$ . For sulphur, e.g., a platelet was made by allowing a melt to cool down slowly, a process that gives the monoclinic form. For the resulting platelet,  $\epsilon$  was measured as the relative capacitance of a Kohlrausch plate condenser ( $C_{\text{sulphur}}/C_{\text{air}}$ ):  $\epsilon = 3.84$  or  $\sqrt{\epsilon} = 1.96$ . The refraction index for monoclinic sulphur was known from the literature:  $n = 2.040$ . The agreement – not too bad, given the tricky nature of the experiment – could be considered as a confirmation (an early one: 1872!) of the postulated equivalence of light and electromagnetism [2]. Boltzmann closely followed the further developments in this domain. Early in 1887 he was one of the first to replicate the revolutionary findings of Heinrich Hertz of the winter before, that is, the production and registration, at a distance,

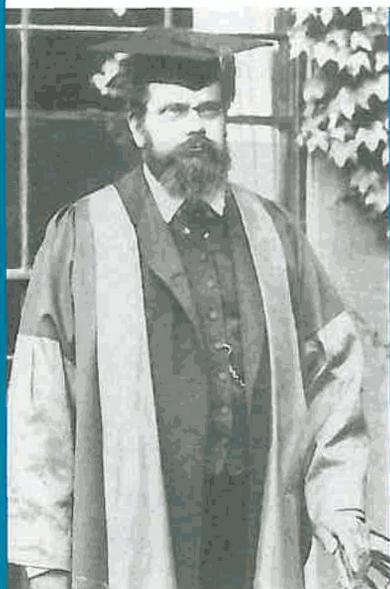
of electromagnetic phenomena of an obviously wave-like nature [3]. Arrhenius and Nernst, as young guests, were among the eyewitnesses.

In a way Clerk Maxwell called the tune. The Scotsman had introduced, in 1860, statistics into the kinetic theory, another fundamental innovation. There had to be a random distribution in the numerical properties of molecules in the gaseous state.

In Maxwell's view this concerned not so much the mass or the diameter, but only the translation velocity. Boltzmann generalized this approach, taking the kinetic energy as the essential variable. The link with thermodynamics was a direct one. When Clausius proclaimed in 1865 that 'The energy of the world is constant; the entropy strives to a maximum', he in fact summarized the First and Second Law. But *entropy* appeared hard to nail down, even for the gaseous state. Boltzmann's colleague Josef Loschmidt, for instance, suggested that since matter, or more particularly a gas, was indeed a huge collection of speedy molecules of ever increasing entropy, then one could reasonably expect at some time in the future the end of the world, a vision with Biblical connotations. The ongoing dissipation of energy would result in what came to be known as the *heat death*. However, since there are evident examples of entropy *decrease* in our environment, there must be some kind of *reverse* mechanism, contradicting Clausius' version of the Second Law. This seemed indeed paradoxical, at least at first sight, as Boltzmann showed in 1877 [4]. The new statistics revealed the answer, though its details were hard to grasp for the, as yet, inexperienced physics community. The probabilities of particular states were the clue: they could be weighted by applying permutation theory, using a discrete model for the energy. For a particular quantity of energy  $L$  divided into a great, though finite, number of 'energy elements'  $\epsilon$  (say  $h$ , such that  $\lambda \epsilon = L$ ) and distributed over, say,  $N$  molecules, a particular number of well-defined distributions would be possible, each of these distributions being realisable in a particular number of ways; each of these ways was called a *complexion*, a wonderful word. Hence, the relative probability  $W$  of a particular distribution could be defined as its number of *complexions*,  $P$  – that is, its *permutability* – divided by the total number of *complexions*,  $J$  ( $= \sum P$ ):

$$W = \frac{P}{J} \quad (1)$$

A given quantity of a gas, in a closed vessel and left to itself, will be in thermal equilibrium. When two (isolated) vessels containing the same gas at the same pressure though at different temperatures are connected, they will tend to straighten out the  $T$  difference. Considering all the possible distributions over the two vessels, it is evident that the initial state has but a poor probability. There are, of course, states of still lower probabilities, e.g. those with greater  $T$  differences. Such a state of greater  $\Delta T$  could of course be attained, at least in principle: Maxwell considered, in 1868, the intervention of an imaginary creature, a *demon*, quick enough to open the stopcock between the vessels when one of the speediest molecules of the colder gas was heading that way. Boltzmann, however, realized that the probability of such an event was very small. He argued that in the succession of molecular events (translation; collisions) the whole is bound to develop in the direction of the most probable distribution, for the simple reason that the number of the latter's *complexions* is by far the greatest. So Loschmidt's argument could be countered: former situations could indeed eventually occur, but the probability of such events was so small, at least in comparison to the overwhelmingly great number of *complexions* of the *most probable* state, that of thermal equilibrium. The same counter-argument applied to Maxwell's demon. Later, Poincaré (1890) and Zermelo (1896) considered another paradox in the



◀ Ludwig Boltzmann as honorary doctor (1894) of the University of Oxford (from [6]).

same vein, that of *recurrence*, implying the regular reappearance of particular states and, implicitly, the periodicity of natural phenomena, more or less in agreement, let's say, with the succession of the seasons. Boltzmann argued that, given the state of thermal equilibrium of the universe as a whole it is doubtless so, that when we, in our corner of low entropy, observe an apparent *increase* which determines our idea of *time*, there will be elsewhere in the universe *decreases* in entropy and a corresponding idea of *time*. The universe considered as a whole, then, tends nonetheless, irreversibly, into the direction of thermal equilibrium. Boltzmann describes all this in terms of his H-theorem, H being a rather arbitrary function which, qualitatively, mirrored more or less Clausius' entropy: H strives to a minimum, where S tends to a maximum.

It was Max Planck who put the intuitively more appealing entropy on a privileged basis. He was to elaborate on Boltzmann's original 'permutation' theoretical approach. In order to account for the *additivity* of entropy, probabilities being multiplicative, the entropy S shows up, with Planck, as a function of  $\log W$ . Since  $\log W$  is dimensionless, then, a proportionality constant k is in the game, giving S the dimension of energy per degree K:

$$S = k \log W \quad (2)$$

This form was proposed in 1900. It allowed Planck to assess the radiation curves of black bodies, which looked like statistical distributions and behaved as such: what Willie Wien (1896) had summarized in his law ( $\lambda_{\max} \cdot T = c$ ) was, conversely, what could reasonably be expected for velocity distributions of a gas at varying temperature. It is fascinating to see how, in various ways, *molecularism* guided Wien and Planck in much the same way: the idea, that is, that the physics and mathematics of the essentially molecular gaseous state may be applied in other domains where discrete entities are at stake. As is well-known, another law, one found empirically by Stefan and claiming that the radiated energy of a cooling body was as the fourth power of its absolute temperature, had been deduced theoretically by Boltzmann (1884).

Boltzmann was a great European scientist, long before Europe became a concrete reality. Broadly educated, he was at ease at the piano – as a pupil of the famous composer Bruckner – and thoroughly familiar with German poetry (Schiller!), occasionally even referring to ancient Greek authors. As a physicist he taught at various universities in Austria-Hungary and Germany. He was otherwise an upright man, on which the socio-political delusions of the day apparently had not the slightest grip. Moreover, his humour and wit are well-documented: the report, for instance, on the *Journey of a German professor into Eldorado, California* is a cheerful case in point. His life, though, ended in a tragedy: on September 5<sup>th</sup> 1906 he took his life while on a medical leave with his family at Duino, near Trieste, Italy. His motivation has puzzled generations of physicists. How could a prominent scientist, member – if not *honorary* member – of the most distinguished Societies of both Europe and the United States, do such a thing? We may add, from this place, that he was nominated several times for the Nobel Prize for Physics, *inter alia* by Planck for those of 1905 and 1906 [5]. There have been rumours about the role of the obstruction with which Boltzmann had had to cope as to his kinetic theory, but, all things well-considered, these were wholly unfounded. The most probable reason were his successive depressions combined with a seriously deteriorating health. He was, for instance, scourged by asthmatic attacks and cartarrh of the nose, and about 1906 his eyes had become so bad that he could hardly read any more: at home, servants were paid for reciting books and the like. On the brink of a new academic year – Boltzmann was to

return to Vienna the next day, September 6<sup>th</sup> – his despair apparently overruled all common sense. His body was repatriated and buried at Vienna's *Zentralfriedhof*: In 1933 a monument was erected, consisting of a bust made by Gustinus Ambrosi in white marble and featuring the entropy formula in the then current form.

### About the author

Henk Kubbinga is a historian of science and technology in the University of Groningen. He passed the PhD (1983) and the 'habilitation' (1996) at the Ecole des Hautes Etudes en Sciences Sociales at Paris. Both theses were published as *L'Histoire du concept de «molecule»* (Springer Verlag, 2001). An abridged Dutch version appeared in two volumes (Verloren Publishers, 2003-2005); an English version, referred to below, is forthcoming.

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### References

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- [1] Max Planck, 'Zur Theorie des Gesetzes der Bnergieverteilung im Normalspectrum', in: *Verhandlungen der Deutschen Physikalischen Gesellschaft* 2 237-245 (1900). Planck wrote  $k = \omega R$ ,  $\omega$  being defined as the mass proportion between 1 molecule and what Planck calls a *g-Molecil*;  $R = 8.31.10$ .
- [2] See particularly: Ludwig Boltzmann, 'Experimentelle Bestimmung der Dielektrizitätskonstante von Isolatoren', in: *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften* (Vienna) 67 17-80 (1873).
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- [5] Elisabeth Crawford, John Heilbron and Rebecca Ullrich, *The Nobel population 1901-1937: a census of the nominators and the nominees for the prizes in physics and chemistry*, University of California Press-Uppsala University Press (1987), p.30 and 32.
- [6] Ilse Maria Fasol-Boltzmann and Gerhard L Fasol (eds.), *Ludwig Boltzmann (1844-1906), zum hundertsten Todesfag*, Springer Verlag (2006).

► Boltzmann preaching the molecular gospel, e.g. at the Lubeck congress of the German Society of Scientists and Physicians (1896), according to a caricature by his student Karl Przibram (1878-1973; 1905) (from [6]).

