Ludwig Boltzmann: a tribute on his 170th birthday

Massimo Falcioni · Angelo Vulpiani

Abstract This is a tribute to Ludwig Boltzmann and a short introduction to some of his many seminal contributions in physics and mathematics (entropy, ergodicity, irreversibility and transport equations).

Keywords Statistical mechanics · Entropy · Irreversibility · Ergodicity

1 Introduction

This article is meant as a small homage to the great Austrian scientist to whom we owe many of the ideas that led to the creation of new research areas in physics and mathematics: a non-exhaustive list includes ergodic theory, large deviations, transport equations and systems with memory (hereditary mechanics). We shall only discuss in detail a few aspects of Boltzmann's contributions, for obvious reasons. Ludwig E. Boltzmann (1844–1906) was born in Vienna on February 20, 1844, the night between Fat Tuesday and Ash Wednesday; he used to say, jokingly, that was the origin of his changes of mood, which swung from moments of sheer enthusiasm to periods of severe depression and eventually led to his suicide in Duino (near Trieste). Boltzmann's stature is unquestionable, yet 170 years after his birth there still are historically inaccurate accounts of his life. The introduction of statistical ensembles, for example, although typically attributed to Gibbs, was actually conceived by Boltzmann. There is no shortage of erroneous opinions—some completely misleading:

Prigogine and Stenger said on many occasions that Boltzmann's ideas were incoherent, if not utterly wrong. Nothing is farther from the truth: Boltzmann's intuitions have been systematically confirmed by a number of detailed mathematical papers and numerical simulations. There is also the fabricated story, groundless, that his depression grew out of unfulfilled academic recognition and the unwelcoming reception of his theories. What is true is that his ideas were vigorously opposed by some, in particular by Mach. However, it is certainly false that those ideas were considered irrelevant: Boltzmann was elected member of the major scientific academies, awarded degrees and doctorates *honoris causa*, received countless invitations to give seminars plus offers of Chairs at leading German universities, which at that time were the most prestigious in the entire world.

2 The life and works

Ludwig Boltzmann (LB) was a restless soul, a generous scientist looking for a tranquility of the mind that he could never find. He moved from one job to the next relentlessly: in 1869 he was appointed professor in Graz, in 1873 he transferred to Vienna, after three years he went back to Graz, and then in 1887—after accepting a Chair in Berlin—he changed his mind and never took it (apparently Berlin's very formal circles scared him). In the letter he wrote to renounce the post he said, rather cheekily, that he did not feel sound enough, mathematically, to accept a Chair in Theoretical Physics. In 1890 he went to Munich, in 1894 to Vienna, in 1900 to Leipzig. He went back to Vienna once again in 1902, and the preparations to have the most renowned Austrian scientist of the time eventually return were massive: this time, though, the Emperor Franz

M. Falcioni A. Vulpiani (✉)
Dipartimento di Fisica, Università degli Studi di Roma
"La Sapienza", Piazzale Aldo Moro 5 00185, Rome
e-mail: vulpiani@roma1.infn.it; angelo.vulpiani@roma1.infn.it

Josef, clearly annoyed by Boltzmann's erratic behaviour, required from him a formal written statement that he would not emigrate yet another time. The comeback was sensational. Boltzmann had two Chairs (Theoretical Physics and Philosophy of Science). The first lecture of the course on philosophy of science was attended by more than 600 people; the largest lecture hall of the university was not big enough so many were force to stand; all newspapers wrote about the event and Boltzmann received the emperor's best wishes. One might think that Boltzmann was an opportunist, that he was after prestigious and well-paid positions, but there is evidence that he did not feel comfortable in the academic world. He was poorly skilled in the 'art of scheming' (in a letter to his mother he wrote of being 'better at integrating [equations] than at intriguing') and he clearly had no great interest in acclaim or reverence. He even refused the noble title the emperor wanted to confer saying 'our bourgeois name was fine for my ancestors and will be fine for my children and grandchildren as well' (Fig. 1).

Despite the many awards he received, and the enormous success of his students (among whom Walther Nernst and Svante Arrhenius, both Nobel laureates for Chemistry, and Paul Ehrenfest), Boltzmann often felt isolated and unappreciated, at least towards the end of his life. What he wrote in the preface to *Lectures on gas theory* (his masterpiece) is telling: 'I am aware that I am only a frail person fighting against the passing of time. But I can give my contribution, so that when the theory of gases will be revived there will not be that much that will need to be rediscovered'.

Fig. 1 Ludwig Boltzman at age 31

Even during difficult times he was quite the fighter, and his confrontations with the opponents of the atomic theory became almost legendary. The most famous incident took place in September 1895 in Lübeck, at the Congress of German Scientists. Years after, Sommerfeld described what happened thus: 'Helm was the champion of energism; then came Ostwald and, afterwards, the philosophical theories of Mach (who was not present at the event). In the opposite corner was Boltzmann, supported by Felix Klein. The skirmish between Boltzmann and Ostwald looked pretty much like a duel between a hefty bull and a trembling bullfighter. Yet on that occasion the bull defeated the man and his agility. Boltzmann's arguments convinced everybody. All young mathematicians like myself were on Boltzmann's side'. After the confrontation in which he was defeated, Ostwald was very upset. The tone of the letter he wrote to his wife is bitter, he mentions 'tight antagonism' and complains that for the first time he 'faced such an openly hostile group of people'. The harsh contention between Ostwald and Boltzmann, who nevertheless remained friends, carried on in a series of papers. Only in 1909 did Ostwald eventually acknowledge that he had been wrong, whilst Mach never backtracked. If he had lived only a few years more LB would have witnessed the full triumph of his work.

Boltzmann was in touch with the major physicists of his times (he wrote to Helmholtz, Lorentz, Planck and Ostwald) and visited the US several times. *Reise eines Deutschen Professors ins Eldorado* (Journey of a German professor in the Eldorado) is an amusing description of the 1905 trip to California. A significant part of the book is devoted to food and beverages. On page one he tells about the last meal in Vienna before departing: 'I ate roasted pork, sauerkraut and potatoes with a few glasses of beer (...) I normally have a good memory, but counting beer pints is somewhat of a challenge'. Californian cuisine was not to his liking: during an official dinner he was served a dish that he thought was more suited for geese, or even worse: 'a Viennese goose would not have deigned to eat this' he was heard to say.

Boltzmann admired the American way of life, which was freer and more democratic than the lifestyle back in the Habsburg empire, but he could not stand the puritanism: 'They hide the wine, as students do with their cigars. This is what they call freedom'. He was disappointed to see that anyone asking directions to a wine store was severely frowned upon, as if he had enquired about 'those ladies'. On his way back to Europe, already far away from puritan America, he cheered up by shunning water completely, and drank only white wine from the Rhine valley.

LB's scientific output was mostly devoted to the construction of a statistical theory capable of describing the behaviour of macroscopic systems, but there are also other

lesser-known yet far from negligible results. We shall briefly overview Boltzmann's contributions to physics.

It is relatively unknown that at the beginning of his career LB worked a great deal on electromagnetism. He was among the first to understand the importance of Maxwell's equations, and in particular the deep connection between optics and electromagnetism. He made detailed measurements of the relationship between the electric constant and the refraction index. Maxwell congratulated him on this and made the young Boltzmann very proud. Following the famous experiments of Hertz on electromagnetic waves LB became so passionate about the subject that in 1886 he repeated the experiments, gave courses on electromagnetism and published his lectures (the two volumes appeared in 1891 and 1893).

In 1872 LB published what is universally known as the Boltzmann equation, which governs the evolution of the probability density of a rarefied gas's velocity, thus recovering in a dynamical setting Maxwell's distribution and the celebrated H theorem. This is the first appearance in the literature of an evolution equation for a probability density. We may also say that it is the first example where probability plays a truly significant role in the natural sciences. Boltzmann's equation, besides representing one of the most elegant and profound chapters of theoretical physics, has seen a host of applications in many scientific and technological fields, from semiconductors to the dynamics of rarefied gases in aerospace engineering.

Boltzmann was one of the forefathers of hereditary mechanics, that is, the study of the effects of memory of past events on the deformations of certain materials, such as glass. In a 1874 paper LB introduces two functions $\phi(t-\tau)$ and $\psi(t-\tau)$ that account for the evolution of the contributions occurred at time $t-\tau$ and inherited, or remembered, at time t. These contributions show up in integral equations that will be developed by Picard and Volterra only at the beginning of the twentieth century.

In 1877 LB published the probabilistic interpretation of thermodynamics, incorporated in the well-known formula $S = k_B \ln W$.

In 1884 he proved the fact, until then only conjectured, that the total energy of a black body is proportional to the fourth power of the temperature, thus confirming the law his teacher, based on experimental observations, had only stated. Although the proof is simple from the mathematical viewpoint, the result is very important because, at the time, thermodynamics was not believed to hold for systems other than gases. In the final decade of the nineteenth century, trying to answer the criticisms raised by Zermelo and Loschmidt, Boltzmann perfected his theory of statistical mechanics and irreversibility and wrote the monumental opus *Lectures on Gas Theory*. He had a great admiration for Darwin, and considered the theory of evolution the

most important discovery of the nineteenth century: 'If someone were to ask me if this century will someday be remembered as the century of steel, steam or electricity, I would answer without a doubt that it will be called the century of the mechanistic view of nature and of Darwin .... In my opinion the entire philosophy of humankind is saved by Darwin's theory'. Boltzmann was very interested in philosophy as well, albeit not in a systematic way (his main fascination clearly remained with physics) and in the final years of his life he gave a course on philosophy of science (of which Mach had been in charge of). Some aspects are extremely intriguing, for they anticipate ideas of Thomas Kuhn on scientific revolutions and paradigms: 'The man on the street might think that new notions and explanations of phenomena are gradually added to the bulk of the existing knowledge (...). But this is untrue, and theoretical physics has always developed by sudden jumps (...). If we look closely into the evolution process of a theory, the first thing we see is that it does not go smoothly at all, as we would expect; rather, it is full of discontinuities, and at least apparently it does not follow the logically simplest path. Sometimes LB has been misunderstood. Popper, for example, although an admirer, accused him of having constructed theories that could not be falsified and called him an idealist. The criticism refers specifically to Boltzmann's computation of the return time $T_R \sim C^N \tau_0$ of a system at microscopic scale, where N is the number of particles, $C > 1$ is a constant and τ_0 a characteristic time. For macroscopic objects, where $N \sim 10^{20}$, the computation gives a time much longer than the universe's age, so Popper believed this was a non-falsifiable hypothesis, in practice: 'I think that [Boltzmann's idea of irreversibility] is completely unsustainable, at least by a realist. It presents the unidirectional evolution as an illusion (...). So it transforms our world into an illusion, together with all our efforts to understand the world better. But eventually it defeats itself (as any form of idealism)'. The accusation is unfair, and wrong: Boltzmann's intuition on return times has been proved rigorously (see Appendix 2). Moreover, if we consider small systems, where N has order 10^1, the problem can be analysed using a computer and the expectations are matched.

It must be said that LB did not make much of an effort to make himself understood; even Maxwell, who shared the same philosophical view, remarked, 'I studied Boltzmann but never fully comprehended him. He did not understand me because of my conciseness, but his verbosity was, and still is, a snag for me'. (Fig. 2).

Boltzmann used to write articles 80–100 pages long and filled with equations, and relegated (often almost hid) the discussion of the important conceptual aspects in few lines. He replied to criticism by saying 'elegance is a matter for

Fig. 2 Boltzmann in later life

tailors and shoemakers'. His style had some enthusiasts, too: a young Albert Einstein, a student at ETH in Zürich at the beginning of the twentieth century, wrote to his girl-friend that he had read Boltzmann and found him magnificent. Despite the high esteem in which he held him, Einstein, too, was well aware that Boltzmann's papers were hard, and admitted that many great physicists had not been able to understand him.

3 The grand vision

The dominant idea in Boltzmann's work was the attempt to reconcile mechanics on the one hand and thermodynamics on the other, that is, to try to build a bridge, both theoretical and concrete, between these two worlds. The road was long and winding, but we can summarise Boltzmann's grand vision in two points:

(I) the introduction of probabilistic ideas and their interpretation in terms of physics;
(II) the quest for a relationship linking the macroscopic world (thermodynamics) to the microscopic one (dynamics).

Point I is extremely delicate and the object of intense study still today. The idea of LB was to substitute time averages with averages coming from a suitable probability density. This conjecture is called the *ergodic hypothesis*. If true, the probability of a region $\mathcal{A}$ in phase space is nothing but the fraction of time spent in $\mathcal{A}$ during the evolution, computed over a very long time.

The relation connecting thermodynamics to the micro-scopic world (engraved on Boltzmann's tombstone) is:

$$S = k_B \ln W,$$

where S denotes the entropy of the macroscopic body (a thermodynamical quantity) and W is the number of microscopic states (a mechanical-like quantity) realising the macroscopic configuration. This law is one of the great achievements of science (on a par with $F = ma$ and $E = mc^2$) and subsumes the large part of statistical mechanics.

3.1 The ergodic hypothesis

If we call $\mathbf{q}_i$ and $\mathbf{p}_i$ the position and momentum vectors of the ith particle, the state of a system of N particles is represented, at time t, by a vector $\mathbf{X}(t) \equiv (\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t), \mathbf{p}_1(t), \ldots, \mathbf{p}_N(t))$ in a $6N$-dimensional space called phase space. The system's observables are functions $A(\mathbf{X})$ defined on the phase space. As particles are subject to the deterministic laws of classical mechanics, $\mathbf{X}(t)$ evolves according to Hamilton's equations. If the Hamiltonian does not depend explicitly on time, the energy is a conserved quantity during motion, and the system moves on a hypersurface of constant energy.

Suppose we measure an observable in thermodynamical equilibrium. It is crucial to notice that the macroscopic time-scale, at which observations are made (order of magnitude 10^{-1}–10^{-3} s), is much bigger than the time-scale of microscopic Hamiltonian dynamics, which governs changes at the molecular level (10^{-11} s). This means that an experimental measurement is, in practice, the result of a single observation during which the system assumes an enormous number of microscopic states. If the datum refers to the observable $A(\mathbf{X})$, it must be compared with the average measured during the system's evolution and taken over a very long time (microscopically speaking):

$$\overline{A}(t_0, \mathcal{T}) = \frac{1}{\mathcal{T}} \int_{t_0}^{t_0 + \mathcal{T}} A(\mathbf{X}(t)) \mathrm{dt}. \tag{1}$$

When we measure the pressure using a manometer, for instance, the result we read is the average over a time $\mathcal{T}$ of the force exercised in the unit of time over the unit of area, with $\mathcal{T}$ depending on the features of the instrument, but certainly much larger than molecular times.

The computation of $\overline{A}(t_0, \mathcal{T})$ for an arbitrary observable requires, in principle, the knowledge of the entire micro-scopic state at a given instant, and also the system's exact trajectory in phase space. This is patently impossible, so if $\overline{A}(t_0, \mathcal{T})$ depended heavily on the initial state of the system, we would not be able to make any guesses at all.

The *ergodic hypothesis* shows us a way out. In essence, it says that any hypersurface of fixed energy is fully accessible to any motion occurring at the given energy level. Said in another way, a constant-energy hypersurface

cannot be divided in regions of finite measure each containing complete motions, i.e. regions invariant under time-evolution (if this is true the hypersurface is called 'metrically indecomposable' or 'metrically transitive'). Furthermore, for any trajectory the average sojourn time in a given region is proportional to the region's volume: hence, there are no 'preferred' regions.

If the above assumption, which represents the core of the ergodic hypothesis, is satisfied, for $\mathcal{T}$ large enough the average in (1) depends only on the system's energy, and therefore it assumes the same value for each evolution with the same energy level; this value, moreover, can be computed by taking an average of $A(\mathbf{X})$ where all states with that given energy (and only these) contribute in the same way. Given that the energy of any system is determined up to a finite error, in the applications it is often useful to average over all states with energy within a certain range. The uniform probability density in the region with energy given up to Δ defines the so-called *microcanonical density*, or *microcanonical ensemble*. Let us denote such density by $\rho_{mc}(\mathbf{X})$ and the volume element in phase space by $d\Gamma = d\mathbf{q}_1 \cdots d\mathbf{q}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N$ (recall that this last is invariant under Hamiltonian motions). Then

$$\rho_{mc}(\mathbf{X}) = \left(\int_{E \le H(\mathbf{X}) \le E+\Delta} d\mathbf{X} \right)^{-1} \equiv (\Gamma_\Delta(E))^{-1}$$

and the ergodic hypothesis allows to write

$$\overline{A} \equiv \lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \int_{t_0}^{t_0+\mathcal{T}} A(\mathbf{X}(t)) dt = \int A(\mathbf{X}) \rho_{mc}(\mathbf{X}) d\mathbf{X} \equiv \langle A \rangle . \tag{2}$$

We remark that the previous equation, if valid, frees us from the need to fix an (initial) state, solve the equations of motion and integrate over time. The *ergodic problem* is precisely the problem of deciding whether (2) holds, in other words whether we can substitute the average of some observable along the time-evolution with an average in phase space. If an isolated system can be described through the microcanonical ensemble, it is not hard to show, for example, that a system with a thermostat is well described by the canonical ensemble. This implies that the proof of (2) justifies dynamically the introduction of statistical ensembles.

We conclude this section by remarking that our presentation does not follow the line of thought of Boltzmann (who changed his mind over the years), but is a modern reconstruction of his ideas.

3.2 The entropy

The microcanonical ensemble defined above is particularly apt for describing the equilibrium of an isolated system, whose thermodynamical state is therefore determined by the energy level (E) and, say, by the volume (V) and the number of particles (N). Suppose the system in question is a gas. In order to establish a link between the statistical and thermodynamical descriptions, it may be convenient to select one particular thermodynamical potential, the entropy (S). We can recover in a rather direct way the entire thermodynamics of the system once we know the expression of S in terms of E, V, N. The rule is precisely the one Boltzmann found:

$$S(E, V, N) = k_B \ln W(E, V, N), \tag{3}$$

where k_B is Boltzmann's constant and $W(E, V, N)$ denotes all microscopic states corresponding to the given equilibrium. In classical mechanics dynamical states constitute a continuous ensemble, so their number must necessarily be a function of the volume in phase space; for this reason the entropy can be defined, in the context of statistical mechanics, as:

$$S(E, V, N) = k_B \ln \Gamma_\Delta(E, V, N) . \tag{4}$$

One motivation for the correspondence comes from Helmholtz's theorem, also known as heat theorem (see Appendix 1).

3.3 Considerations on ergodicity

The ergodicity issue for a macroscopic system, apart from being a hard problem to solve, might also be irrelevant in the context of statistical mechanics. Because of the large number of particles, and the consequently very big size of the phase-space regions, the time $\mathcal{T}$ necessary for the two averages in (2) to be comparable (provided they are indeed equal) might exceed the age of the universe, *at least for some observables*. In this situation $\mathcal{T}$ would not have any physical interest, nor would Eq. (2). Deciding how large $\mathcal{T}$ is, so that $\overline{A}(t_0, \mathcal{T})$ be close to $\langle A \rangle$, is therefore an important point. We expect that the answer to this question, in general, will depend both on the observable A and on the number of particles N. At this stage we have to remark that the relevant observables in thermodynamics, those characterising equilibrium states, are not arbitrary functions. They are few and of a very special kind; the physically interesting question is whether the times to reach an equilibrium (the equality between averages in time and phase space) are short enough for these functions. As a matter of fact Eq. (2) can be recovered from the following considerations:

(a) in macroscopic systems the number of microscopic constituents is very large;

(b) the interesting point in statistical mechanics is to look at (2) not for generic observables but in relationship to the few observables relevant in thermodynamics (such as kinetic energy, pressure,

density) having a special structure: namely, those that can be expressed, exactly or with good approximation, as sums of the microscopic constituents' separate contributions;

(c) it is acceptable that (2) might not hold for initial conditions in regions of overall small measure (tending to zero as $N \to \infty$);

(d) it is acceptable for (2) to hold approximately:

$$\left| \overline{A} - \langle A \rangle \right| < \epsilon$$

with ϵ tending to zero as $N \to \infty$.

These physical requirements are not so binding mathematically, and Khinchin proved that for all macroscopic systems studied in thermodynamics one can obtain interesting results, even if not as general as the ergodic theorems, that hold for arbitrary dynamical systems of even low dimension, for arbitrary observables and for almost any initial condition.

It is useful to emphasise two facts about this restricted framework:

- dynamics does not play an essential role: for the interesting observables the existence of good statistical properties on any constant-energy hypersurface does not depend on the dynamical details, but is related to the fact that $N \gg 1$.
- interesting observables are usually (macroscopically) constant *on most* of the constant-energy hypersurface, *but not everywhere*; this fact allows non-equilibrium states to exist in this picture;

The next step, to substantiate the idea of equilibrium and to make the framework coherent, is to prove that if we start from a non-equilibrium state, then Hamiltonian dynamics makes the system evolve in the 'right direction' (Boltzmann equation).

3.4 The role of dynamics

When a system with given energy is initially in a non-equilibrium state, which occupies a 'small' portion of the hypersurface, we expect the evolution to move it to the equilibrium region, which has biggest volume. We will show, using a simplified situation, that the expected behaviour is a consequence of the laws of dynamics.

One first step in this direction was made by LB with his transport equation (simply known as *Boltzmann equation*). He was trying to tackle the following problems:

(a) obtain, within Newtonian mechanics, the Maxwell–Boltzmann (MB) distribution for the velocity of the molecules of a gas in thermodynamical equilibrium (we will explain later that additional assumptions are needed to accompany the laws of dynamics);

(b) show, within classical mechanics, that a generic probability distribution tends asymptotically to the MB distribution.

The basic idea is to study the behaviour in time of a particular 'collective' variable, which provides partial information on the system's microscopic state: this is the distribution $f_X(\mathbf{q}, \mathbf{p})$ of molecules in the various single-molecule states. By definition, $f_X(\mathbf{q}, \mathbf{p}) \, d\mathbf{q} \, d\mathbf{p}$ represents the number of molecules that are in one of the states contained in the volume element $d\mathbf{q} \, d\mathbf{p}$ around the point $(\mathbf{q}, \mathbf{p})$ in the phase space of the single molecule, for a given state $\mathbf{X}$ of the system. Let us emphasise that this function, as signalled by the subscript X, is defined on states $\mathbf{X} \equiv (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$ of systems of N particles. As f_X is a density in the single-molecule's phase space, $f_X(\mathbf{q}, \mathbf{p})/N$ represents an 'empirical' probability density in terms of the microscopic state $\mathbf{X}$. The function f_X depends upon time, as a function of the state $\mathbf{X}$ whose evolution is governed by the Hamiltonian equations.

Boltzmann considered diluted gases, whose density is low and temperature high. He wrote the transport equation by starting from an exact evolution equation for a generic $f_X(t)$ and introducing the *molecular chaos* assumption (which will be discussed below). From Boltzmann's equation it follows that:

(a) there exists a stationary solution $\hat{f}$ given by the MB distribution;

(b) the evolution takes every $f \neq \hat{f}$ towards $\hat{f}$.

Boltzmann's equation describes the 'right' behaviour of $f_X(t)$ but carries an additional non-dynamical hypothesis with it (*molecular chaos*). This flaw was eliminated in the 1970s using *Lanford's theorem*. Assuming molecules to be hard balls, this result shows that in the Boltzmann–Grad limit (well suited for describing diluted gases) the evolution of a given f_X, for short times, is governed exactly by Boltzmann's equation in the majority of the states X it represents: this number is as close to the total as one wants, provided one considers sufficiently many molecules.

All this shows that the basic ideas for explaining the thermodynamical behaviour of macroscopic systems from microscopic equations are solidly rooted in the theory, at least for a given system and within a certain limit.

More will be said about Boltzmann's equation below.

3.5 E. Boltzmann's equation and the H theorem

Let us consider a gas of N identical particles of mass m contained in a box (of volume V) with elastic and smooth walls (or periodic boundary conditions). The particles are subject to:

(I) an external force $\mathbf{F}(\mathbf{x})$ acting on the single particle at $\mathbf{x}$;

(II) a short-range coupling interaction, non-zero only for $|\mathbf{x}_i - \mathbf{x}_j| \leq \sigma$. We may for instance think of a gas made of hard balls of radius r whose potential is ∞ if $|\mathbf{x}_i - \mathbf{x}_j| \leq 2r$ and zero if $|\mathbf{x}_i - \mathbf{x}_j| > 2r$.

We further assume the gas is diluted, that is, that σ is much smaller that the typical distance $\ell = (V/N)^{1/3}$ between particles.

Let us reconsider the distribution $f(\mathbf{x}, \mathbf{v}, t)$ introduced earlier, which multiplied by $d\mathbf{x} d\mathbf{v}$ gives the number of molecules of velocity $\mathbf{v}$ at $\mathbf{x}$ at time t. In this section, as was customary in the past, we think of f as a function of $(\mathbf{x}, \mathbf{v})$ instead of $(\mathbf{q}, \mathbf{p})$, as the formalism of analytical mechanics would traditionally dictate; we have also suppressed the index X to simplify the notation.

The evolution equation for f reads:

$$\frac{\partial f}{\partial t} + (\mathbf{v} \cdot \nabla) f + \left(\frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}}\right) f = C \tag{5}$$

where $\nabla_{\mathbf{v}}$ is the gradient with respect to the velocity components and C is the contribution coming from particle interaction. In absence of interactions $C = 0$ and (5) becomes

$$\frac{\partial f}{\partial t} + (\mathbf{v} \cdot \nabla) f + \left(\frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}}\right) f \equiv \frac{Df}{Dt} = 0. \tag{6}$$

where D/Dt is the total derivative along the trajectory, and expresses the conservation of density f. Assuming for simplicity that there are no external forces, and neglecting the spatial dependence of f, Eq. (5) reads

$$\frac{\partial f}{\partial t} = C. \tag{7}$$

For diluted gases it suffices to consider the variation due to binary collisions, as the contribution of multi-particle collisions (triple and so on) can be disregarded. The equation can be written in this form:

$$\partial_t f(\mathbf{v}_1, t) = \int W[(\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)]\{F^{(2)}(\mathbf{v}_1', \mathbf{v}_2', t)$$
$$- F^{(2)}(\mathbf{v}_1, \mathbf{v}_2, t)\} d\mathbf{v}_1' d\mathbf{v}_2' d\mathbf{v}_2, \tag{8}$$

where $W[(\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)]$ accounts for the cross section of the given transition and $F^{(2)}(\mathbf{u}, \mathbf{v}, t) d\mathbf{u} \, d\mathbf{v}$ is the number of pairs with given velocities. It is important to point out that the explicit expression of $W[(\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)]$ is in many respects irrelevant; for example, for the stationary distribution's expression and for the H theorem. The (necessary) appearance of $F^{(2)}$ makes the system not closed, and we must describe the evolution equation for $F^{(2)}$; this entails introducing a new function $F^{(3)}$, whose

evolution requires an $F^{(4)}$ and so on (this is the problem of the BBKGY hierarchy, a common feature of all nonlinear problems). Boltzmann's hypothesis (usually called *molecular chaos assumption*, 'Stosszahlansatz' in German) factorises $F^{(2)}(\mathbf{v}_1, \mathbf{v}_2, t)$ as product $f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)$:

$$\partial_t f(\mathbf{v}_1, t) = \int W[(\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)]\{f(\mathbf{v}_1', t) f(\mathbf{v}_2', t)$$
$$- f(\mathbf{v}_1, t) f(\mathbf{v}_2, t)\} d\mathbf{v}_1' d\mathbf{v}_2' d\mathbf{v}_2. \tag{9}$$

Introducing the function

$$H(t) = \int d\mathbf{v} f(\mathbf{v}, t) \ln f(\mathbf{v}, t), \tag{10}$$

as $W[(\mathbf{v}_1', \mathbf{v}_2') \to (\mathbf{v}_1, \mathbf{v}_2)] \geq 0$ and $(\ln x - \ln y)(x - y) \geq 0$ for every $x > 0$, $y > 0$ it is easy to prove that $dH/dt \leq 0$. What is more, (9) implies that $dH/dt = 0$ only if the $f(\mathbf{v})$ solve

$$f^{(s)}(\mathbf{v}_1) f^{(s)}(\mathbf{v}_2) = f^{(s)}(\mathbf{v}_1') f^{(s)}(\mathbf{v}_2'). \tag{11}$$

or equivalently

$$\ln f^{(s)}(\mathbf{v}_1) + \ln f^{(s)}(\mathbf{v}_2) = \ln f^{(s)}(\mathbf{v}_1') + \ln f^{(s)}(\mathbf{v}_2'). \tag{12}$$

Since equal particles in an elastic collision satisfy $|\mathbf{v}_1|^2 + |\mathbf{v}_2|^2 = |\mathbf{v}_1'|^2 + |\mathbf{v}_2'|^2$, it follows that a generic initial probability distribution $f(\mathbf{v}, 0)$ tends to the MB distribution: $f^{(s)}(\mathbf{v}) \propto \exp -[m|\mathbf{v}|^2/2k_B T]$. If we set the entropy S proportional to $-H$, it will never decrease and will have a maximum corresponding to the MB distribution. At this point it would seem that the H theorem provides a 'proof' of the second law of thermodynamics—one of the cornerstones of macroscopic physics—in terms of kinetic theory. That we wrote 'proof' indicates that things are not quite that easy...

3.6 Two apparently hopeless paradoxes

The solution proposed by Boltzmann to the problem of irreversibility clashes with the recurrence paradox (due to E. Zermelo) and the reversibility paradox (due to J. Loschmidt). Zermelo noticed that the H theorem disagrees with Poincaré's recurrence theorem, whereby in any mechanical system whose motion takes place in a bounded region of phase space, at some finite time T_R the system will return arbitrarily close to the initial conditions. Since the distribution function f, and thus H, depend on the position and velocity of the molecules, when the system returns to the initial state, H, too, must reach a value arbitrarily close to the initial value. Consequently $H(t)$ cannot be a monotone function of time.

Now to the reversibility paradox: if H decreases from time 0 to time t, and at t the velocities are reversed, then

because of the time-symmetric nature of the equations of motion the system will go back after t, and H should increase. The main tool for addressing the objections to the H theorem is to clarify the latter's authentic meaning: this is not a theorem of classical mechanics, and hence does not hold for any solution of the equations of motion. According to Boltzmann, 'the second law [of thermodynamics] cannot be deduced mathematically from the equations of dynamics alone (...). What I proved is that it is highly likely that $H(t)$ will approach its minimum; if it is bigger, it can either increase or decrease, but the probability that it will decrease is [much] higher'.

Boltzmann managed to give a preliminary answer to the paradoxes uncovered by Zermelo and Loschmidt (and later his arguments would be proved to be essentially correct).

As for the recurrence paradox, he pointed out that if we are given a non-equilibrium microscopic state $\mathbf{X}(0)$, associated to the distribution $f(0)$, at some later time T_R the state $\mathbf{X}(T_R)$ will be close to $\mathbf{X}(0)$, and hence $f(T_R)$ will be 'close' to $f(0)$; but Poincaré's return time is for macroscopic systems extremely long, and *de facto* not observable. For example, before one cubic centimetre of gas at normal pressure and temperature returns to the original state (allowing a measurement error of 10^{-9} m on the position and 1 m/s on the velocity), we would have to wait something like $10^{10^{19}}$ years, an eternity in comparison to the universe's age. Nowadays Boltzmann's argument is subsumed by Kač's lemma (see Appendix 2).

We come now to the second paradox, which can be presented as follows. States $\mathbf{X}(0)$, represented by the distribution $f(0)$, occupy a volume $\mathcal{V}(0) \sim \exp^{\{-H[f(0)]\}}$ in phase space; as $\int f(\mathbf{x}, \mathbf{v})\, d\mathbf{x}\, d\mathbf{v} = N$, we have $H \propto N$. In the diluted-gas limit (Boltzmann-Grad), the majority of states, after a period t, will be well represented by $f(t)$, the solution to the Boltzmann equation with initial datum $f(0)$; therefore $H[f(t)] < H[f(0)]$. Hence the volume occupied by states represented by $f(t)$, i.e., $\mathcal{V}(t) \sim \exp^{\{-H[f(t)]\}}$, is much bigger than $\mathcal{V}(0)$. If we now take $f(t)$ as new (non-equilibrium) initial condition, the majority of states in $\mathcal{V}(t)$ will be governed by the equation (with a further decrease of H); the fraction of states—negligible just like $\mathcal{V}(0)/\mathcal{V}(t)$—for which that fails contains both states evolved from $\mathbf{X}(0)$ and states obtained from the latter by reversing velocities at time t. The 'anti-H' behaviour of the paradox cannot be excluded, but it may occur only by an extremely accurate preparation of the microscopic state (one that reverses, at time t, the velocities of all particles exactly and simultaneously). It is practically impossible to obtain such a behaviour by a random choice of initial conditions compatible with the given $f(t)$; the probability of preparing a state in $\mathcal{V}(t)$ with 'anti-H' evolution has order $\mathcal{V}(0)/\mathcal{V}(t) \sim \exp^{\{-|H(t)-H(0)|\}}$, which is exponentially small in N since $|H(t) - H(0)| \propto N$.

Finally, we note that it is easy to prove that in presence of molecular chaos, as in the vast majority of states represented by a given $f(t)$, $H(t)$ has a local maximum, and the reversibility paradox does not apply to initial conditions where $H(t)$ has a maximum point, as Boltzmann pointed out.

The argument leads to the unsettling observation that $H(t)$ has (mostly) 'peaks' and at the same time is a decreasing function; within simplified probabilistic models it is possible to prove that Boltzmann's intuition is essentially correct (and rigorous in a suitable limit).

The greatness of Boltzmann's work comes not so much from having 'reduced thermodynamics to mechanics', as some claim; rather, it lies in the explanation that irreversibility cannot be understood solely with the laws of mechanics. He made us comprehend the subtle nature of the emergence of irreversibility, for which two fundamental ingredients are necessary:

(a) a large number of particles (atoms or molecules), which is at the heart of the substantial imbalance between the microscopic and macroscopic scales;

(b) suitable initial conditions (those generating molecular chaos): the laws of mechanics have nothing of the kind of the second law of thermodynamics, which can be reduced to mechanical terms only by means of special assumptions on the initial conditions.
We may add to these a third element (somehow related, and complementary, to (b)):

(c) the use of probability: not all microscopic states evolve in an irreversible way, but only 'most of them'. With macroscopic systems, where the number of particles is enormous, it is practically certain that an irreversible behaviour will be seen.

Boltzmann's approach is probabilistic, which implies that the second law of thermodynamics must lose (at least conceptually) the status of absolute law to become a probabilistic event. After a long journey strewn with controversies and debates, Boltzmann grasped (and had some explanation for) the fact that mechanical reversibility is not at odds with thermodynamical irreversibility.

In contrast to the section on ergodicity, the previous discussion is faithful to Boltzmann's original thoughts (albeit presented using contemporary language).

4 The decisive (posthumous) triumph

LB's scientific legacy is gigantic: his ideas were the starting point for whole new areas of mathematics (like the theory of large fluctuations); they influenced Planck's study of black bodies, and provided the foundations of the modern techniques of numerical simulation (see Appendix 3). Even

Fig. 3 Boltzmann's tomb in Vienna

the controversial aspects of his approach have been clarified, thus showing that his intuitions were eventually correct (Fig. 3).

4.1 Brownian motion

Boltzmann did not manage to convince all his critics that atoms exist as physical entities, and not just as a useful hypothesis for computations, as Mach believed when he said 'the atomic theory plays in physics a role similar to certain mathematical concepts; it is a model to help figuring out certain facts.' By the 1910s the last opponents had given up (not Mach): during a 1911 congress in Paris, where he was summarising Einstein's work on Brownian motion, Arrhenius declared 'after this we can no longer question the essentiality of the existence of atoms'. Atoms really exist even if we cannot see them (as Mach liked to say), and Perrin had in fact counted them using Einstein's formula on Brownian motion.

A macroscopically tiny but microscopically huge object like a pollen grain, when immersed in a liquid, zig-zags in a highly irregular way: the motion has very precise properties statistically speaking. If we observe one spatial component long enough we have:

$$\langle [x(t) - x(0)]^2 \rangle \simeq 2Dt,$$

where $\langle \; \rangle$ indicates an average, for instance over a large number of grains. As Einstein proved in his *annus mirabilis* (1905):

$$D = \frac{T\mathcal{R}}{6\pi\eta a N_A}$$

where D is the mass diffusivity while $\mathcal{R}$, η, T, a and N_A are the gas constant, the viscosity, the temperature, the particle's (pollen's) radius and the Avogadro number. Brownian motion is a superb magnifying glass on the microscopic world, and enables us to detect relationships between macroscopic quantities as $D, \mathcal{R}, \eta, T, a$ (accessible experimentally), and microscopic quantities such as the Avogadro number N_A.

Apparently LB was not aware of Einstein's 1905 work on Brownian motion. It is interesting that Einstein did not care about the phenomenon in itself, his real purpose being to show that 'in agreement with the molecular theory of heat, bodies visible under the microscope and suspended in a liquid possess a movement so evident that it can be observed. Possibly, the phenomenon I am talking about is related to so-called Brownian motion.' In other terms he wanted to find, using statistical mechanics, the experimental evidence proving the existence of atoms, in line with Boltzmann.

4.2 Mathematical developments of Boltzmann's equation

The technical machinery needed for proving the H theorem in a suitable limit is impressive. Starting from a pivotal 1948 paper by Grad we have eventually arrived at stating, and proving, what Boltzmann's profound physical insight had envisioned. Among the many people that have taken part in this enterprise we mention Illner, Lanford, Shinbrot, Di Perna, Lions, Pulvirenti and Cercignani. The essence of their work may be summarised as follows:

In Grad's limit:

$$N \to \infty, \quad \sigma \to 0, \quad N\sigma^2 \to constant, \tag{13}$$

where N is the number of molecules per unit of volume and σ their diameter, the probability of having molecular chaos tends to 1 (absolute certainty) if the system's initial condition is not in thermodynamical equilibrium and $f(\mathbf{x}, \mathbf{v}, t)$ evolves according to Boltzmann's equation, so that the H theorem holds.

The physical meaning of Grad's limit becomes clear if we observe that while the total volume $N\sigma^3$ tends to zero and the gas becomes very diluted, the interactions survive and allow for a finite variation of f, since the single-collision's cross section is proportional to σ^2 and the time derivative of $f(\mathbf{x}, \mathbf{v}, t)$ is a multiple of $N\sigma^2$.

For gases Grad's limit is physically realistic: at normal temperature and atmospheric pressure, for instance, $1\,\text{cm}^3$ contains $N \sim 10^{20}$ molecules and $\sigma \sim 10^{-8}\,\text{cm}$, so

$N\sigma^2 \sim 1\,\mathrm{m}^2$; the volume occupied is small compared to the total volume, for $N\sigma^3 \sim 10^{-4}\,\mathrm{cm}^3$.

It is really impressive how well this result agrees with Boltzmann's intuition.

Translated from the Italian by Simon G. Chiossi.

Appendix 1: Helmholtz's cycles and some ideas of Boltzmann on ergodicity

Boltzmann's journey towards a consistent formulation of statistical mechanics starting from mechanics was long and tortuous. Today we summarise the overall achievement with two (apparently independent) facts:

- the ergodic hypothesis;
- the law relating entropy to mechanics: $S = k_B \ln W$.

There is an interesting relationship between ergodicity and the entropy-volume formula. It is based on a result of Helmholtz for one-dimensional Hamiltonian systems, which seems to be unknown even to those interested in the history of physics. Luckily it was recently exhumed by Gallavotti, and discussed with extreme clarity by Campisi and Kobe (see Appendix 4, "For further reading"). To present it briefly, consider a one-dimensional mechanical system with Hamiltonian

$$H(q,p,V) = \frac{p^2}{2m} + \phi(q,V)$$

where V is a control parameter that can vary, e.g., the length of a pendulum. Assuming the potential $\phi(q,V)$ diverges as $|q| \to \infty$, the motion will be periodic for any value of E and V. Denote by $\tau(E,V)$ the period, and by $q_-(E,V)$, $q_+(E,V)$ the minimum and maximum values of q. The system is obviously ergodic: as the motion is periodic, during the evolution the system visits the entire phase space of given energy, and an easy computation shows that the time and microcanonical averages coincide provided we use the measure

$$d\mu(p,q) = \frac{\delta(H(q,p,V) - E)dqdp}{\int\int \delta(H(q,p,V) - E)dqdp}. \tag{14}$$

We have the following result

Helmholtz theorem. Define temperature and pressure in terms of time averages $\langle \ldots \rangle_t$ by:

$$T = \frac{2}{k_B}\left\langle \frac{p^2}{2m} \right\rangle_t, \quad P = -\frac{1}{k_B}\left\langle \frac{\partial\phi(q,V)}{\partial V} \right\rangle_t \tag{15}$$

and set

$$S(E,V) = k_B \ln 2 \int_{q_-(E,V)}^{q_+(E,V)} \sqrt{2m[E - \phi(q,V)]}dq. \tag{16}$$

Then

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad \frac{\partial S}{\partial V} = \frac{P}{T}. \tag{17}$$

Note that $S(E,V)$ can be written in the usual form

$$S(E,V) = k_B \ln \int_{H(q,p,V) < E} dpdq. \tag{18}$$

Helmholtz's theorem implies a highly non-trivial fact: namely, that there is a mechanical analogue of the second law of thermodynamics. If T and P are given by time averages of mechanical quantities, the expression

$$\frac{dE + PdV}{T}$$

is an exact one-form.

Boltzmann's idea was to generalise this to multi-particle systems and find a function $S(E,V)$ for which (15) and (17) would hold. By assuming ergodicity on a system of N particles (the periodic evolution in dimension one is replaced by a motion that visits the entire constant-energy hypersurface) one can prove a generalised Helmholtz theorem; the proof does not depart much from the one-dimensional situation, but now we have

$$S(E,V) = k_B \ln \int_{H(\mathbf{q},\mathbf{p},V) < E} d\mathbf{q}d\mathbf{p}.$$

instead of (18). This definition of entropy is still not quite (4), but the two expressions practically coincide when $N \gg 1$.

In terms of cycles the ergodic hypothesis essentially consists in assuming that the trajectory will sweep the whole surface $H = E$. Therefore, replacing the time average with the microcanonical average is completely natural.

Appendix 2: Return time and Kač lemma

Poincaré's recurrence theorem says nothing about how long the return time might be. The issue is addressed by Kač's lemma:

In an ergodic system the average return time in a region A is

$$\langle \tau_A \rangle = \frac{\tau_c}{\mu(A)},$$

where τ_c is a characteristic time and $\mu(A)$ the measure of A.

To understand how difficult it is to observe recurrence we might consider a D-dimensional system; the probability

$P(A)$ of sojourning in a region A with normalised size ϵ in each direction is $P(A) \sim \epsilon^D$, so

$$\langle T_R \rangle \sim \epsilon^{-D}.$$

Since a macroscopic system of N particles has $D = 6N$ already at low precision (e.g. 10%, that is for $\epsilon = 0.1$), the average return period is $O(10^{6N})$. Assuming $N \sim 10^{23}$ the average return is $\sim \tau_c 10^{10^{23}}$, irrespectively of τ_c. This is far longer than the age of the universe, a dwarf at a 'mere' $\sim 10^{10}$ years $\approx 10^{17}$ s. Kač's lemma is a direct consequence of ergodicity. The proof is easy for systems with discrete states, like Markov chains, with invariant probabilities $\{P_k^*\}$. In that case the return time of a system initially (time 0) in state m is

$$\langle T_m \rangle = \frac{1}{P_m^*}. \tag{19}$$

Let τ_1 denote the time needed to return for the first time to m, τ_2 the second return time and so on. After $\mathcal{N}$ iterations, a period

$$t_{\mathcal{N}} = \sum_{n=1}^{\mathcal{N}} \tau_n$$

has passed and the system has been in state m for this fraction of time:

$$f_{\mathcal{N}} = \frac{\mathcal{N}}{t_{\mathcal{N}}}.$$

Ergodicity implies

$$\lim_{\mathcal{N} \to \infty} f_{\mathcal{N}} = P_m^*, \quad \lim_{\mathcal{N} \to \infty} \frac{t_{\mathcal{N}}}{\mathcal{N}} = \langle T_m \rangle,$$

and then (19) follows.

Appendix 3: Simulations à la Boltzmann in statistical mechanics

The ergodic hypothesis is, strictly speaking, false. This is confirmed by a series of mathematical results, like the KAM theorem (after Kolmogorov, Arnold, Moser), as well as by numerical simulations, first and foremost the work of Fermi, Pasta and Ulam. A very interesting result in physics is due to Khinchin, who proved how systems with many degrees of freedom satisfy a slightly weaker form of ergodicity: in a nutshell, ergodicity holds for a special class of physically important functions, provided we exclude 'small' regions (of negligible measure) in phase space.

Despite these *caveats* ergodicity has many undoubted merits. First of all, it allows introducing probability in the framework of deterministic systems in a natural way. In particular, as ergodicity is equivalent to the assumption that different trajectories have the same asymptotic features, we have a means to interpret probability in frequentist terms. With ergodicity, the probability of an event (defined via its asymptotic frequency) is an objective and measurable property: it suffices to follow a trajectory long enough. We insist on the fact that we are talking about a single system (even if with many degrees of freedom) and not of a collection of identical systems. By adopting Boltzmann's point of view, it is natural to believe that the only statistical approach that is physically sound (at a theoretical level) is the one where time averages are taken along the time evolution of the system.

This is exactly what numerical simulations do (Monte Carlo methods, or molecular dynamics), and is also what happens in the laboratory.

Let us now rapidly discuss how ergodicity is employed in numerical simulations. Consider a system of N particles of mass m subject to an external potential U_e (generated, say, by the walls of the container). The particles interact under a coupling potential that depends on the distance $U(r)$, and the system is described by the Hamiltonian function

$$H = \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m} + U_e(\mathbf{q}_j) \right] + \sum_{i,j} U(|\mathbf{q}_i - \mathbf{q}_j|).$$

The vector $\mathbf{X} = (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)$ evolves under the Newtonian dynamics

$$m \frac{d^2 \mathbf{q}_j}{dt^2} = \mathbf{f}_j(\mathbf{Q})$$

where $\mathbf{Q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ and $\mathbf{f}_j$ is the total force acting on particle j. Clearly, the previous equations do not have an analytic solution. The idea behind *molecular dynamics* is conceptually simple: given an initial condition $\mathbf{X}(0)$ one wants to find numerically the trajectory $\mathbf{X}(\Delta t), \mathbf{X}(2\Delta t), \ldots, \mathbf{X}(k\Delta t), \ldots, \mathbf{X}(\mathcal{M}\Delta t)$, where Δt is the integration interval, and then compute statistical averages over $\mathcal{T} = \mathcal{M}\Delta t$:

$$\bar{A}^{\mathcal{T}} = \frac{1}{\mathcal{M}} \sum_{k=1}^{\mathcal{M}} A(\mathbf{X}(k\Delta t)).$$

If $\mathcal{T}$ is large, ergodicity says that the time average will approach the average of the microcanonical density; thus we can reconstruct thermodynamics from dynamics. For instance: given an energy level E we can determine the temperature $T(E)$ (with the average kinetic energy), and repeating with other energies we find the specific heat C_v:

$$\frac{1}{C_v} = \frac{\partial T(E)}{\partial E},$$

and hence the entropy

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v dT}{T}.$$

Molecular dynamics enables us to determine accurately the thermodynamical properties of a system starting from its Hamiltonian (i.e. the microscopic interactions), and it was employed successfully in fluid dynamics.

We conclude by mentioning in passing that molecular dynamics, which is based on the idea that the statistical properties generated by dynamics represent the core of a physical phenomenon, is not just a tool that spits out numbers. Sometimes numerical simulations are true experiments that make it possible to discover phenomena that are not obvious or even in contrast to established ideas. The most notable example is the experiment that Fermi, Pasta and Ulam carried out in the 1950s using one of the first non-military computers. The experiment, simulating a chain of particles linked by springs with weakly non-harmonic potentials, showed how a small perturbation of an integrable system is not sufficient to make a system ergodic (in contrast to what physicists believed at the time). Another example of some physical interest is the presence of so-called hydrodynamic tails: in liquids certain correlation functions do not decay exponentially (as long believed), but as a power law.

Appendix 4: For further reading

There are English translations of the most important book by Boltzmann and also a good selection of popular articles that provide a rather exhaustive picture of his philosophical position:

- L. Boltzmann, *Lectures on Gas Theory*, Dover Publications, 2011.
- L. Boltzmann, *Theoretical Physics and Philosophical Problems*, ed. Brian McGuinness, Springer, 1974.

The figure of Boltzmann the physicist and the philosopher (and the times in which he lived) is described in a wonderful book, full of valuable information:

- C. Cercignani, *Ludwig Boltzmann: The Man Who Trusted Atoms* (Oxford University Press 1998).
- C. Cercignani, *Boltzmann, un genio nell'Austria felix* (i Grandi della Scienza, n 33, maggio 2003, Le Scienze).

A nice collection of articles on several technical and conceptual aspects is:

- G. Gallavotti, W.L Reiter and J. Yngvason (eds.), *Boltzmann's Legacy*, (European Mathematical Society, 2008).

For a presentation (in some places historically inaccurate, but still faithful) of Boltzmann's ideas in statistical mechanics see

- P. Ehrenfest and T. Ehrenfest, *The Conceptual Foundation of the Statistical Approach in Mechanics* (Cornell University Press, 1956; German original from 1911).

A nice textbook on statistical mechanics that collects a number of accurate contributions (often with an unconventional approach) written for the Enciclopedia Treccani

- G. Gallavotti, *Statistical Mechanics. A Short Treatise* (Springer-Verlag, Berlin 1995).

A lucid presentation of Helmholtz cycles and the relationship to ergodicity can be found in:

- M. Campisi and D. Kobe, "Derivation of the Boltzmann Principle", Am. J. of Physics **78**, 608 (2010).

For a short discussion on the Fermi-Pasta-Ulam experiment and its relevance in statistical mechanics:

- M. Falcioni and A. Vulpiani, "Enrico Fermi's contribution to non-linear systems: the influence of an unpublished article" in *Enrico Fermi: his work and legacy*, C. Bernardini and L. Bonolis (eds.), p. 271 (SIF and Springer-Verlag, 2004).

The classic textbook on limit theorems for computing probabilities in statistical mechanics, and the ergodic hypothesis from a physical viewpoint is:

- A.I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, (Dover Publications, 1960).

For irreversibility theorems, Boltzmann's equation, a discussion on paradoxes and stochastic models the reader should definitely read:

- M. Kač, *Probability and Related Topics in Physical Sciences*, (Am. Math. Soc. 1957).

For chaos, coarse graining and the many degrees of freedom of statistical mechanics:

- P. Castiglione, M. Falcioni, A. Lesne and A. Vulpiani, *Chaos and coarse graining in statistical mechanics*, (Cambridge University Press, 2008).

A detailed study of the technical and conceptual aspects of the foundations of statistical mechanics:

- N. Zanghì, *I fondamenti concettuali dell' approccio statistico in fisica*, in *La Natura delle Cose* V. Allori, M. Dorato, F. Laudisa and N. Zanghì (eds.), (Carocci, Roma 2005).

On Boltzmann and biology:

- P. Schuster, "Boltzmann, Atomism, Evolution, and Statistics", *Complexity* **11**, 9 (2006).

A passionate reconstruction of the origins of Brownian motion and the computation of the Avogadro number:

- J. Perrin, *Les Atomes*, (Alcan, Paris 1913); English translation: *Atoms*, (Van Nostrand, 1916).

Something more recent:

- L. Cohen, "The History of Noise", *IEE Signal Processing Magazine*, November 2005 p. 20.
- A. Baldassarri, A. Puglisi, D. Villamaina and A. Vulpiani, "Relazione fluttuazione—dissipazione: una finestra sul mondo microscopico", *Lettera Matematica Pristem* **77**, 21 (2011).
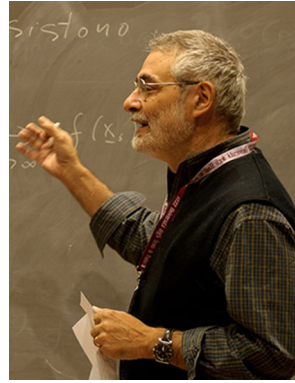
Angelo Vulpiani is a Professor of Theoretical Physics at the University of Rome "La Sapienza" and is a Fellow of the Institute of Physics. He has been visiting scientist in Belgium, Denmark, France, Sweden and U.S.A. His research interests are statistical mechanics, dynamical systems, turbulence, transport, and reaction-diffusion processes.
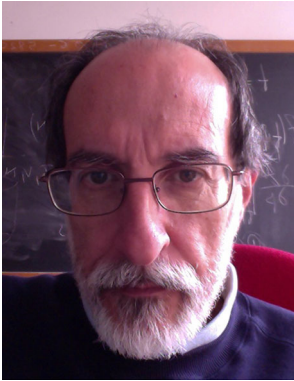
Massimo Falcioni is a Professor of Statistical Mechanics at the University of Rome "La Sapienza". His research interests are statistical mechanics, dynamical systems, chaos and complexity.