

$$\frac{i\hbar \partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \Psi + V\Psi$$

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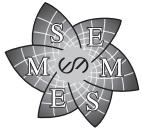
# Boltzmann's Legacy

Giovanni Gallavotti  
Wolfgang L. Reiter  
Jakob Yngvason

Editors



European Mathematical Society





*Ludwig Boltzmann*

Ludwig Boltzmann (1844–1906)

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# Foreword

To commemorate the 100th anniversary of Ludwig Boltzmann's death in Duino the Erwin Schrödinger International Institute for Mathematical Physics invited eminent scientists to meet in the city where Boltzmann was born and where he spent a good part of his life as a student and scholar. The International Symposium "Boltzmann's Legacy", held from 7 to 9 June, 2006 at a lecture hall devoted to his memory, the Boltzmann Lecture Hall, brought together scholars from all over the world whose scientific achievements bear evidence to Boltzmann's everlasting and fundamental contributions into the development of science.

Legacies can both be a source of delight and a burden and this two-sidedness is particularly apparent in Boltzmann's case. His scientific work is a highlight of the natural sciences at the turn of the 19th century: controversial at his time, and to this day both a delight and burden for the scientists following his steps. Boltzmann was a genuine philosopher-scientist, a superb mathematician as well as a physicist, and in his later life also a philosopher. He was a scholar still deeply rooted in the Newtonian tradition during its final turn. Today his heroic fight for "mechanics" sounds alien to us. As the prophet of the new paradigm of statistical mechanics, his insights deeply influenced his followers. Although Boltzmann's work is formulated in the language of classical physics it reaches into the post-classical era of quantum physics and relativity theory, personalised by Planck and Einstein.

Boltzmann was a bullish fighter with a delicate skin. This deeply troubled man and thinker, fighting against the ailments of his body and soul, finally ended his life tragically in Duino on September 5, 1906. He achieved the deepest insights into some burning problems of physics that were ripe to be tackled by a genius. The invention of the equation that bears his name and deals with the time-development of statistical ensembles is one of his well-known masterpieces. The Boltzmann constant that links the microscopic with the macroscopic is perhaps the most frequently used constant in all of physics. To paraphrase the saying attributed to Newton, one might say that a good part of theoretical physics sits on the shoulders of this giant.<sup>1</sup> The Erwin Schrödinger Institute could be regarded as his youngest Viennese brain child sitting conscientiously on his shoulders watching out.

Clearly, the importance and eminence of Boltzmann's revolutionary achievements have reached far beyond his life time. He is one of the rare species of scholars whose ideas are still as vivid today both in a constructive and controversial way as they had been during his life span. The contributions collected in this volume give a keen picture of the fertility of Boltzmann's legacy.

What made the Symposium "Boltzmann's Legacy" such a delight felt by all participants, were the vivid and often emotional debates signalling the fecundity and omnipresence of Boltzmann's ideas. We hope that reading the articles collected in this

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<sup>1</sup>Robert K. Merton, *On the Shoulders of Giants. A Shandean Postscript*. New York: The Free Press 1965.

volume will give a flavour of the spirit which guided the presentations.

The editors are deeply indebted to the contributors of this volume, for their willingness to put in writing their presentations at the Symposium, as well as enduring the subsequent tedious interventions by the editors.

We thank the University of Vienna's Central Library for Physics for providing photos. We are especially grateful to Boltzmann's granddaughter, Mrs. Ilse M. Fasol-Boltzmann, for permission to reproduce photos held in the possession of her family.

The Symposium was generously supported by the Rektor of the University of Vienna, Professor Georg Winckler. The co-operation with the City of Vienna's lecture series "Vienna Lecture" and of Professor Hubert Christian Ehalt in organising a public lecture for Jürgen Renn is gratefully acknowledged.

We owe special thanks to Mrs. Irene Zimmermann for many valuable suggestions and her proofreading of all the papers during the final stage of the preparation of the volume. Finally, we wish to thank Manfred Karbe of the European Mathematical Society Publishing House for his support and constant help in producing this volume.

At various stages during the preparation of this volume the editors observed how difficult it is to easily get access to the original papers of Ludwig Boltzmann. Even the three volumes of the *Wissenschaftliche Abhandlungen*, a collection of 139 of his papers, edited by his pupil and successor Friedrich Hasenöhrl, are missing in some important libraries.<sup>2</sup> It was felt by all participants of the Symposium that the availability and an easy access to his writings would be extremely useful and even a *conditio sine qua non* for a proper understanding of his legacy. Following the encouragement of one us (G. G.) the Erwin Schrödinger Institute – in the spirit of "Boltzmann's Legacy" – intends to produce a freely available and electronically accessible version of the *Wissenschaftliche Abhandlungen* together with the *Populäre Schriften*<sup>3</sup> on the web. This service will be in the honour of the work and memory of Ludwig Boltzmann.

Vienna and Rome, August 2008

Giovanni Gallavotti  
Wolfgang L. Reiter  
Jakob Yngvason

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<sup>2</sup>L. Boltzmann, *Wissenschaftliche Abhandlungen*, (F. Hasenöhrl, ed.). J. A. Barth: Leipzig 1908, 1909, 3 volumes; reprinted Chelsea Publishing Company: New York 1968, 3 volumes, reprinted by the American Mathematical Society in 2001.

<sup>3</sup>Ludwig Boltzmann, *Populäre Schriften*. J. A. Barth: Leipzig 1905.

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# Introduction

Giovanni Gallavotti

On the occasion of the 100th anniversary of Ludwig Boltzmann's death in 1906 Vienna's prestigious scientific institutions were certainly an appropriate setting for a commemorative event dedicated to illustrate his legacy by presenting comments on his pioneering work and developments.

Boltzmann has been a key figure in the development and eventual acceptance of atomism: although his insights into the structure of matter have certainly vindicated Democritus' early intuitions it should be stressed that his work has been influential far beyond statistical mechanics. In physics on quantum mechanics [1], and on gas and plasma theories, for instance; in mathematics on dynamical systems and ergodic theory [2], and the analytic theory of Boltzmann's equation has been a challenging problem (starting already with Hilbert [3]); in engineering the equation became and remains an essential tool, from aeronautical and aerospace projects to reactor design [4], [5]. In philosophy he often took unorthodox but stimulating views; after 1884 he made efforts to popularize his science and devoted substantial time to counteract the critical objections to his theory of irreversibility. The articles collected here in the form of proceedings, and the talks presented at the conference but not recorded here, touched many aspects of Boltzmann's scientific achievements and life.

Conceptual revolutions have the feature of being remarkably susceptible to different interpretations, sometimes even contradictory and nevertheless being fertile to prepare the ground for new developments. Thus Boltzmann can be seen as having marked the high point of a mechanistic view of the world before its decline [Renn]<sup>1</sup>, or as having strengthened it [Lebowitz, Cohen]; and within each view important differences of interpretations emerge. Furthermore, neither viewpoint really fits well with quantum mechanics nor can it explain, satisfactorily by today's standards, "simple" physical properties like the Fourier's or Ohms's laws [Lieb].

Quantum mechanics was influenced since the beginning by Boltzmann's statistical mechanics, starting with the works of Planck and Einstein but also of Bose, Pauli, Fermi and Dirac, to name only some of the first few. Historians of science have even gone as far as thinking that he was inadvertently using quantum mechanics, when he was imagining the phase space as discrete and composed of cells of equal phase space volume [6]. This does not seem to be right, however, because if this had been the case Boltzmann would not have escaped to notice the consequence that temperature would not be identifiable with kinetic energy and equipartition could not hold [Lieb]; two properties that play a central role in his approach [7].

His influence is particularly felt in contemporary attempts to understand nonequilibrium phenomena, and equilibrium as well if seen as a particular case of the former. Boltzmann asked the question whether there could be several models of macroscopic

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<sup>1</sup>Names in square brackets [name] refer to the authors of the subsequent articles in this volume.

thermodynamics, arriving at the conclusion that there are different statistical ensembles, but they lead to the *same* macroscopic thermodynamics. Here I refer to his paper of 1884 [2], where the “ergodic hypothesis” received the current name, although it had been formulated earlier [8], together with Maxwell, giving rise to the modern branch of mathematics called ergodic theory. The 1884 paper might be considered the apex of his original production [9]. Even now we ask the further question whether equilibrium thermodynamics, *i.e.* the thermodynamic potentials and their universal relations, can be derived from assumptions which need not appeal to a microscopic dynamics based on indivisible objects and whether such a purely macroscopic, classical, approach leads to a unique determination of the potentials (and to their identity with the derivation from the theory of the ensembles introduced by Boltzmann) [Lieb].

The heritage of the 1884 paper has been taken up by the modern works on nonequilibrium and, not surprisingly, research in this direction bifurcates while attempting to extend the notion of some of the thermodynamics functions, primarily entropy, to nonequilibrium situations. Here sometimes radically different objectives are achieved. For instance, the attempt to make precise the notion of coarse graining can lead to an extension of Boltzmann’s entropy formula (that he only formulated for (very) dilute gases, in his  $H$ -theorem), to a formula which applies to general macroscopic assemblies of particles evolving classically and extends considerably the  $H$ -theorem [Lebowitz].

It can, however, also lead to the conclusion that entropy cannot be defined (uniquely) in nonequilibrium situations, even if stationary [Cohen]. Nevertheless, evolution might still be controlled by a Lyapunov function giving a measure of how far an evolving system is away from the eventual stationary state, at least in systems with chaotic enough time evolution [Gallavotti] (without contradicting the above extension of the  $H$ -theorem, but not allowing in general the interpretation of the Lyapunov function as a function of the macroscopic state, whether evolving towards stationarity or already there). The second viewpoint is inspired by Ruelle’s theory of turbulence and its relation to generic properties of dynamical system [10], a theory that can also ultimately be traced back to Poincaré and Boltzmann.

There seems to be a rather general consensus that the question is “to what extent can a system evolving according to Newton’s laws be modeled by a random system?” [Ornstein]. The ideas concerning turbulence developed into a “Gordian knot” approach called the “chaotic hypothesis” [Gallavotti, Cohen], but there are several important issues which require further research [Ruelle], particularly if the question is asked in a quantum mechanical context replacing “Newton” by “Schrödinger” [Ruelle, Lieb]. Nevertheless, something close to the chaotic hypothesis is known to hold in rather simple, yet physically interesting, systems: the hard core gases, whose theory is well developed and is closely related to information theory (via “Kolmogorov’s entropy”) and to some of the most interesting results on coding theory and on dynamical systems equivalence (or “isomorphism”) [Ornstein].

The approach to equilibrium is, of course, a part of nonequilibrium statistical mechanics and once more Boltzmann is the founder of another important chapter, based on “Boltzmann’s equation”: the equation is tantalizing for its derivation of irreversibility from mechanics.

This is a success story and a chapter where substantial understanding has taken place, with the proof of the validity of Grad's conjecture for short times by Lanford more than six lustres ago. The discussion in [Cercignani] is concluded by pointing out that the mathematical theory of the equation is still quite primitive, because a solution algorithm for it is not yet available ("solution algorithms" are often the physicists' name for "uniqueness theorems" in analysis), in spite of the early attention given to the problem by mathematicians (*e.g.* Hilbert [3]) and physicists (*e.g.* Chapman and Enskog [11]).

Nevertheless, the mathematicians efforts have generated many developments [Villani] in which the notion of entropy is repeatedly used in the form of a convenient *a priori* estimate for studying various nonlinear PDE's. It also arises in non-commutative measure theory *i.e.* in von Neumann algebras) and in the related non-commutative probability theory. In physics, Boltzmann's equation has been exploited for the practical need of studying gases and plasmas; but it also served in the fundamental problem of deriving hydrodynamic equations: a programme started with the empirical expansions of Hilbert and Chapman–Enskong and recently pursued in a modern, mathematically precise form [Villani].

In technology, Boltzmann's equation is widely applied; as examples I mention here the linear version for neutron diffusion in a reactor [5], or the full nonlinear version employed in gas flows (or, more precisely, the numerical codes believed, on experimental grounds, to be related to it: because, I stress again, no solution algorithm is known for it, nor for its "consequences", the hydrodynamic equations [Cercignani, Villani])

Nontrivial extensions of Boltzmann's equation, regarded as an equation describing "collision" events that can be considered as occurring randomly and independently, have been developed following his idea of representing them via scattering cross sections. This has arisen, for instance, in the phenomenological theory of crystal oscillations (where the colliding objects are phonons) and in electric conduction theory (where the colliding objects are electrons). Beyond phenomenology it had applications also in mathematical physics to study nonlinear wave equations where the nonlinearity is represented in generating collisions between free traveling waves. A substantial understanding of nonlinear phenomena in simple equations, like the cubically nonlinear wave equation [Spohn], ensued.

The dynamical foundations of statistical mechanics remain of central interest: until very recently extensions of Boltzmann's  $H$ -theorem to interacting matter, originally for very weakly interacting systems has not met real success, neither in nor out of equilibrium, in spite of criticism and demands, for instance from Einstein, to base it on dynamics [Cohen]. The situation is changing now [Lebowitz], but the lively discussions on this point that took place at the meeting were unfortunately not taped.

Not unexpectedly (perhaps) new developments came from observations made possible by the ever increasing power of electronic computations. They led to the discovery of even more phenomena to be explained, and at the same time realized the strong and extremely fruitful link between dynamical systems and statistical mechanics along the lines parallel to the ones advocated, since the early 1970s, in the theory of turbulence

[Ruelle]. With the necessity of interpreting results of simulations as coarse grained representation of motion, which can be formulated rather precisely for chaotic systems [Gallavotti], this led to a few nontrivial applications (the Fluctuation Theorem and its consequences), beyond the realization that the Gibbs equilibria are special cases of a much more general class of stationary distributions on phase space, the SRB distributions [Cohen, Ruelle].

The role of computer simulations has therefore been essential and the theoretical consequences seem to have gone, so far, beyond reasonable expectations. As in all developments that proceed too fast, greatly many papers have been generated together with a great number of misunderstandings. The rapid pace of electronic communication amplified the impact of a superficial study of other scientists' work and led to a remarkable confusion between very different results and, eventually, to mistakes passing unchecked into publications in respected journals. The quotation of Boltzmann in footnote<sup>31</sup> of [Renn] is quite appropriate here. The problem seems to be that the basic (but wrong) assumption is, in many cases, that nothing can be really interesting or not known in others' work to be worth taking away time that could be spent more profitably on computers.

A refreshing review about the role of computer simulations [Dellago and Posch], in particular concerning the century-old questions of the macroscopic and microscopic properties of equilibrium distributions, should therefore not have been absent. The problems of the time scales and the irreversibility phenomenon can now be studied in quite a detail, pursuing the early analysis of Thomson [12] and Boltzmann [13], which came too early to be really understood at that time, surprisingly not even by Poincaré who has to be counted, together with Maxwell and Boltzmann, among the founding fathers of the subject. This it is becoming more and more apparent now from the role played by dynamical systems in statistical mechanics. The fractals, certainly conceived by Poincaré, are believed to play a role even in systems like a gas in a container. This is a (controversial) point that can be studied in simulations and is analyzed in [Dellago and Posch] while raising the question: "What if Boltzmann had a computer?" (which does not lead to the answer of the verger to an analogous question in W. Somerset Maugham's short story, as I would have feared, given the dangerous nature of computers).

Mathematically rigorous theorems about dynamics of large assemblies of particles are a daunting task. Very few results can be established, but this does not mean that attempts are lacking, and a few remarkable achievements stand. Besides the already mentioned proof of Grad's conjecture, the time evolution in a few systems has been shown to be stable as their size increases (at given density of matter and energy). This means that if a system is large enough the trajectories of a finite number of particles, located at a finite distance from the origin and observed for an arbitrarily *prefixed time*, cease to depend on the system size, and this happens with a probability approaching certitude at least if measured with respect to an equilibrium Gibbs distribution (for some potential, not necessarily the one controlling the motion). This is due, under reasonable assumptions on the interaction potentials (among which are short range and superstability), to the important property that dynamics takes place "by clusters".

If a time  $t$  is fixed, the set of particles that up to  $t$  affect each other's motion and contain a given particle  $P$  is called the cluster of  $P$  and it is isolated (*i.e.* at distance greater than the range of the potential and up to time  $t$ ) from the remaining particles. Once it is established that, for fixed  $t$ , the particles can be collected in clusters, non interacting up to time  $t$  (a property first proposed by Bogolyubov), many questions can be raised. For instance, in the case of hard spheres, how fast does the number  $N$  of particles in a cluster ("cluster size") grow with time, starting from  $N = 1$  at time  $t = 0$ ? This can be studied in simulations [Gabrielov et al.], and surprises come from the detection of what are likely to be the first genuine phase transitions and scale phenomena which develop, in particle systems, as *time* (rather than as usual, say, temperature or density) grows beyond a critical value  $t_c$ . Again we see how increasingly computers power affects our work.

It is well known that Boltzmann had strong interest in Darwin's evolution theory. However it is unlikely that he could foresee that in just a century computer simulations of evolution processes could become possible, and to a large extent informative. This is now happening [Schuster], and there is a large amount of freedom in selecting models, which are maps or differential equations, conceptually often stemming from the ideas that lead to the original derivation of Boltzmann's equation: this opens broad horizons for the future of biophysics.

In conclusion a short account of Boltzmann life, and of his views on life and philosophy, had to be given a prominent place in a commemoration [Renn, Reiter]. His life, that could have been extremely happy and quiet seen from an outsider's viewpoint, was not such. He was restless, and he was not at all a happy man in his private life in spite of being surrounded by a loving family.

He took positions that were not always popular and defended them successfully, not only in physics but also in other disciplines like philosophy. His arguments were often too advanced for his audience [Reiter].

This meant that they had to be repeated over and over again which has been, then and later, erroneously attributed to a lack of confidence on his part about his own work. The conceptual difficulty of his ideas, due to their originality, has not been eased by the 20th century physicists (nor mathematicians) who, in their majority, relied on second hand accounts of his work [7].

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# Boltzmann and the end of the mechanistic worldview

Jürgen Renn

## Introduction

When historians of science look back at the turn of the 20th century in order to understand the beginnings of modern physics they mostly think about the revolutionary work of Albert Einstein. Would he indeed not be a better subject to discuss the end of the mechanistic worldview than Ludwig Boltzmann? As a matter of fact, however, Einstein's revolution of his miraculous year 1905 cannot be understood if one does not take into account what Boltzmann had achieved beforehand. Curiously, when Einstein was appointed to the Prussian Academy of Sciences in Berlin in 1912/13, the physical chemist Walter Nernst dubbed him *Boltzmann redivivus*, for Einstein's appointment was above all due to his work on atomism, on the theory of heat, and on statistical physics, that is, Boltzmann's main fields of activity. From Boltzmann, who was not blessed with a miraculous year, we can learn much about what excellent science really is beyond such singularities. One can learn from Boltzmann, for example, that Einstein's quote about fantasy being more important than knowledge does have its limits, and that years of hard work and endurance are sometimes more important than brief flashes of genius. One of the first things one learns as an historian of science, however, is that flashes of genius like the ones that hit Einstein in 1905 are inconceivable without long years of preliminary work, and that he, as Newton expressed it, was in fact able to see further because he stood on the shoulders of giants like Ludwig Boltzmann.

Perhaps Boltzmann provides a better model for us today than Einstein, because Boltzmann's work marks the end of an epoch characterized by a seemingly accomplished worldview based, however, on daring conceptual constructions such as the aether. Similarly, the solutions we think we've found for many fundamental problems in our current scientific worldview work only with the aid of such artificial hypotheses. In the area of cosmology, for instance, concepts such as dark matter and dark energy are strongly reminiscent of the fabulous constructs of classical physics that characterized the end of the mechanistic worldview, to which, beyond the aether, mechanical atomism also belongs. Perhaps today we require conceptual changes as radical as those that caused the transition from the mechanistic worldview to the theories of relativity and modern quantum physics.

Boltzmann's name is typically associated with Vienna although a closer look shows how he was a world citizen. It is true, Boltzmann's relationship with Berlin was one of rather mixed feelings. Looking back on his years in Berlin, he later recalled that a single glance from Helmholtz made clear to him that joviality and humour did not

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This text is based on a lecture held in Vienna on June 7, 2006. A German-language version has been published in the book series "Wiener Vorlesungen im Rathaus", Band 130, herausgegeben für die Kulturabteilung der Stadt Wien von Hubert Christian Ehalt: Jürgen Renn, *Boltzmann und das Ende des mechanistischen Weltbildes*, Wien: Picus Verlag, 2007. The English translation was prepared by Susan Richter.

befit a learner there. But although he loved his Austrian homeland, Boltzmann was no fanatic nationalist. His patriotism was directed above all to the Viennese way of life. Thus he once remarked on the feeling that overcame him before a major journey, “No Viennese is unmoved when eating the last goulash with dumplings and, while the Swiss concentrates his homesickness in the memory of cow herds and cowbells, the Viennese yearns for *Geselchtes mit Knödel*.<sup>1</sup> However much he may have loved *Geselchtes*, Boltzmann was an open-minded man who loved his freedom. He was in America three times, and made an honest effort to learn English. Here a small sample from his memoirs of the *Reise eines deutschen Professors ins Eldorado*, as his travelogue is entitled:

“My English conversation proceeded according to this scheme. Me: When lunch will be served? Him: ieeöö. Me: I beg you, could you say me, at what hour lunch will be served? His gurgling a fifth lower: aoouu. I grasp what is amiss in my plan of attack and yell frantically: Lönch, lanch, lonch, launch etc. I produce vowels that would be sought in vain in Gutenberg’s typesetting case. Now his face shows some sign of comprehension; Ah, loanch? Now the bridge of understanding has been built. Me: When? at what hour? When o’clock? Him: Half past one! We understood each other. And now I was supposed to hold thirty lectures in this language.”<sup>2</sup>

As far as Boltzmann’s love of freedom is concerned, in his famous travelogues he cites Schiller approvingly: “Just another couple thousand guys like me, and Germany should be transformed into a republic that makes Rome and Sparta look like nunneries.”<sup>3</sup> Indeed, today the Federal Republics of Austria and Germany are truly anything but nunneries.

Despite his tragic death, Boltzmann was basically an optimist who believed in progress, not only with a view to the development of society, but above all with a view to science, where this optimism was rather more justified, although further scientific progress was not entirely possible without ruptures and revolutions either.

But how does such a scientific optimism strike us from today’s perspective? Does he seem merely naïve, or did Boltzmann already presage the great breakthroughs of the twentieth century? Such a retrospective on his own expectations for the future could have appealed to Boltzmann. As he once wrote, “I find it peculiarly attractive to imagine how happy the pathbreaking geniuses of the most varied fields would be at the achievements of their successors who in many ways stood on their shoulders; for example, what would Mozart feel today if he could hear a master performance of the Ninth Symphony or of Parsifal? The great Greek philosophers of nature and above all that ardent mathematical genius, Archimedes, would have said roughly the same to the achievement of present-day technology [...]”<sup>4</sup>

Such a retrospective is all the more interesting because the scientific progress Boltzmann had set his stakes on also overturned much of *what he himself* believed. Thus it

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<sup>1</sup>Boltzmann, Ludwig: “Reise eines deutschen Professors ins Eldorado”. In: Boltzmann, Ludwig. 1925. *Populäre Schriften*. 3. ed. Leipzig: Verlag von Johann Ambrosius Barth, p. 404.

<sup>2</sup>Ibid., p. 412.

<sup>3</sup>Ibid., p. 417.

<sup>4</sup>“On the Principles of Mechanics.” In: Boltzmann, Ludwig. 1974, pp. 129–152, p. 148.

seems worthwhile to take a closer look at Boltzmann's scientific credo, his vision of a physical worldview, not least because this could help us to answer questions about the structure of scientific revolutions that we cannot answer from the study of the revolutionaries alone, whose very achievement lay in overthrowing such a credo.

I will first elaborate the vision that provided the conceptual framework for the difficult and persistent work that ultimately created the prerequisites for the later revolutionaries. Then I will submit a proposal for how scientific revolutions can be understood and finally, against this background, endeavour to acknowledge Boltzmann's achievements and his contributions to the overthrow of the mechanistic worldview, followed by a brief description of each of these contributions.

## The dual Boltzmann

A closer look at the conceptual background of Boltzmann's work yields an ambivalent impression. I will designate this ambivalence by referring to a first and a second perspective.

**Boltzmann: the last representative of the mechanistic worldview.** From the first perspective, Boltzmann appears as the last representative of a doomed, centuries' old scientific research program, which unfolds in the context of a mechanistic worldview and endeavours to integrate non-mechanic phenomena like heat phenomena using the idea of mechanical atoms. Boltzmann himself thus wrote, "It is the ubiquitous task of science to explain the more complex in terms of the simpler [...] Therefore in physics too the attempt was made to reduce all other phenomena, such as sound, light, heat, magnetism and electricity, to mere motions of the smallest particles of these bodies, and this turns out quite successful for very many phenomena, although of course not for all. Thus the science of motion, that is mechanics, became the root of the other physical disciplines, which seemed increasingly to grow into special chapters of mechanics."<sup>5</sup>

Although critique of this vision intensified toward the end of the nineteenth century, Boltzmann held to it fast, writing, "The possibility of a mechanical explanation of all of nature is not proven, indeed, it is hardly conceivable that we will achieve this goal completely. Yet neither is it proven that we will not still make great progress in its direction, and consequently enjoy its benefits in manifold ways."<sup>6</sup>

He believed that his position toward his critics was similar to Galileo's when he defended the Copernican theory against the dogmatism of the Catholic Church that the Earth moved around the Sun. According to the legend, Galileo grumbled after being condemned by the Inquisition: And yet it does move! So Boltzmann, too, after forty years of work on atomistic explanations of heat phenomena, in particular for gases, formulated in 1897, "Yet I am confident that I can say of the molecules: And yet they do move!"<sup>7</sup>

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<sup>5</sup>Ibid., p. 149.

<sup>6</sup>Idem: "Ein Wort der Mathematik an die Energetik." In: Boltzmann 1925, pp. 104–136, p. 136.

<sup>7</sup>Idem: "Über einige meiner weniger bekannten Abhandlungen über Gastheorie," *Verhandlungen der 69. Versammlung Deutscher Naturforscher und Ärzte*, Braunschweig 1897, p. 19. (*Jahresbericht der Deutschen Mathematischen Vereinigung* 6 (I), 130 (1899)). Reprinted in: L. Boltzmann, *Wissenschaftliche Abhandlun-*

From this first perspective Boltzmann was one of the last defenders of the mechanistic worldview, and did indeed see himself as one of the last defenders of atomism. As such, he wrote in the foreword to the second part of the second edition of his lectures about gas theory, “In my opinion it would be [...] a detriment for science if gas theory were to fade into obscurity for a time through the currently prevailing mood so hostile to it, as, for instance, undulation theory once did through the authority of Newton. I am well aware how powerless the individual remains against the currents of time. But still, in order to do what I can to contribute to a situation in which not all too much must be rediscovered when gas theory is picked up again, in this book I included even the most difficult parts of gas theory, which are most subject to misunderstandings, and attempted to present at least their fundamentals in as easily comprehensible a manner as possible.”<sup>8</sup>

Similarly, in his lecture about the development of the methods of theoretical physics of 1899, after sketching the state of theoretical physics at the beginning of his studies, he wrote, “How many things have changed since then! Indeed, when I look back on all these developments and revolutions I feel like a monument of ancient scientific memories. I would go further and say that I am the only one left who still grasped the old doctrines with unreserved enthusiasm – at any rate I am the only one who still fights for them as far as he can. I regard as my life’s task to help to ensure, by as clear and logically ordered an elaboration as I can give of the results of classical theory, that the great portion of valuable and permanently usable material that in my view is contained in it need not be rediscovered one day, which would not be the first time that such an event had happened in science. I therefore present myself to you as a reactionary, one who has stayed behind and remains enthusiastic for the old classical doctrines as against the men of today; but I do not believe that I am narrow-minded or blind to the advantages of the new doctrines [...].”<sup>9</sup>

Boltzmann was well aware of the difficulties presented by the purely mechanical explanation of magnetism and of electricity, and also proved sceptical toward speculative atomism. So he wrote, “We must further admit that the orientation of research that I have called classical theoretical physics led to occasional excrescences against which a reaction was necessary. Every Tom, Dick and Harry felt the call to excogitate some structure, some vortices and concatenations, of atoms, believing thereby to have spotted the Creator’s plan once and for all.”<sup>10</sup>

Boltzmann believed that he was surrounded by critics, or at least by opponents of the atomic hypothesis. But who were his critics, what did they want, and what did Boltzmann think of them? Were *they* perhaps the true revolutionaries who were to shape the future of physics? They were indubitably prominent. A number of them, as Boltzmann,

<sup>gen</sup>, Verlag J. A. Barth, Leipzig: 1908, 1909, vol. 3, p. 598.

<sup>8</sup>Idem: “Vorlesungen zur Gastheorie. II. Teil. Vorwort.” In: Idem: *Vorlesungen über Gastheorie*, I. und II. Teil. Einleitung, Anmerkungen und Bibliographie von Stephen G. Brush. Vol. I of the Ludwig Boltzmann Edition, edited by Roman Sexl, Graz: Akademische Druck- und Verlagsanstalt, p. v f.

<sup>9</sup>Idem: “On the Development of the Methods of Theoretical Physics in Recent Times (1899)” (Lecture held at the Munich Naturforscherversammlung, 22 September 1899). In: Boltzmann 1974, pp. 77–100, p. 82.

<sup>10</sup>Ibid., p. 93.

were both physicists and philosophers: Wilhelm Ostwald, Ernst Mach, Pierre Duhem and Georg Helm. In the final decade of the nineteenth century their ideas determined the zeitgeist – against speculative conceptions – for a physics oriented purely on the phenomena, which renounced invisible mechanisms and instead relied on structural similarities in the behaviour of energy. Their vision was rather that of a methodological unity of physics, with which they replaced a uniform physical worldview on the basis of mechanics. Boltzmann himself characterized them thus: “one had become suspicious of all hypotheses and confined the task of theory to supplying a description of phenomena without anywhere going beyond what was given by experience.”<sup>11</sup> He took no stock in such caution, especially when, as in the case of Mach, it was linked with an exclusive emphasis on sensory impressions and mental acts as the actual substance of physical knowledge. He could only make fun of such a self-restriction of physics. Thus he wrote with irony, “When I say that foreign countries and people exist, the conceptual core of this is actually the mere fact that certain energetic acts, which are called acts of volition (stamping a ticket, entering a railroad car, etc.) consequently, and contradictable only temporarily by closing one’s eyes, falling asleep, or after a long series of mental acts (the return trip), are followed by an enormous abundance of new ideas, which are predictable with wondrous accuracy through a map, timetable, etc.”<sup>12</sup>

It was the unholy alliance between a philosophy thus self-restricted and the hope, which Boltzmann was convinced was short-sighted, of securing the conceptual unity of physics with the help of the energy concept – a concept that spanned all sub-areas of physics – against which Boltzmann directed his conception that he must preserve the fertility of mechanistic heuristics for coming centuries, just as in his view it would have been better had Newton’s particle theory not temporarily displaced wave theory.

Yet if one looks more closely, his ambitions appear far greater: Boltzmann believed that mechanics would provide the foundation for any scientific explanation of the world. So he wrote, “The god by whose grace the kings rule is the fundamental law of mechanics.”<sup>13</sup>

And similarly, in his inaugural lecture in Leipzig of 1900: “In nature and art the all-powerful science of mechanics is thus ruler, and likewise in politics and social life.”<sup>14</sup> From his perspective, topics like the emergence of life, the way the drives and passions function, were part of a mechanistic worldview, as were logic and the mechanisms of social institutions. Thus he wrote on the theory of evolution, “We must mention also that most splendid mechanical theory in the field of biology, namely the doctrine of Darwin.”<sup>15</sup>

He concerned himself with mechanistic speculations about the emergence of life: “We frame the hypothesis that complexes of atoms had developed that were able to multiply by forming similar ones round them. Of the larger masses so arising the most viable were those that could multiply by division, and those that had a tendency to move

<sup>11</sup>Idem: “On the Principles of Mechanics.” In: Boltzmann 1974, p. 144.

<sup>12</sup>Idem: “Zur Erinnerung an Josef Loschmidt.” In: Boltzmann 1925, pp. 228–252. p. 247.

<sup>13</sup>Idem: “On the Principles of Mechanics.” In: Boltzmann 1974, p. 136.

<sup>14</sup>Ibid., p. 135.

<sup>15</sup>Ibid., p. 133.

towards places where favourable conditions for life prevailed.”<sup>16</sup>

Sometimes, however, it is not entirely clear how seriously Boltzmann’s enthusiasm for the mechanistic worldview should be taken, for example, when he writes, possibly with an ironic reference to the complex social machinery of the Austro-Hungarian Empire, “We must further call to mind how well all the mechanism of social arrangements too fits into the framework of these considerations. There we find countless rules of propriety and forms of politeness that seem, in part, so unnatural and forced that they seem absurd and ridiculous to that unprejudiced view often called reason but which in fact involves a forgetfulness of the omnipotence of mechanics [...] but exist they must.”<sup>17</sup>

And occasionally, he even treated his students in accordance with the image of mechanics, as he writes himself in his Leipzig lecture, “Finally, a word to you, my future pupils and student colleagues: be full of idealism and enthusiasm in absorbing everything that your alma mater offers you, but in assimilating it be mechanical and go on working untiringly and uniformly like machines.”<sup>18</sup>

But ultimately, over and again the profound conviction shines through that he is on the right path, the path of completing a mechanistic worldview in which atomism plays a key role. “present day atomism is a perfectly apt picture of all mechanical phenomena, and given the closed nature of this domain we can hardly expect it to throw up further phenomena that would fail to fit into that framework.”<sup>19</sup>

In summary, from this first perspective one has the impression of looking at a world long past, like reading Thomas Mann’s *Magic Mountain*, at a world that was doubtlessly extremely creative, but just as doubtlessly fated to certain doom.

**Boltzmann: pioneer of modern physics.** While the perspective of Boltzmann as protagonist of a nearly forgotten world naturally suggests itself to the historian of science who wants to understand scientific achievements from within their own age, a different perspective suggests itself to the physicist of today, namely that of Boltzmann as a pioneer of modern physics, whose achievements are timeless and whose accomplishments were enduring and path-breaking, such as those leading to today’s statistical mechanics, or others that even helped to pave the way for quantum theory and the theory of relativity in both its special and general forms. Taking all of this into consideration, the fact that we are dealing not with a physicist of today, but one from the nineteenth century ceases to be relevant and reduces to a question of local colour.

Among Boltzmann’s enduring accomplishments are, above all, his contributions to gas theory. His scientific work in this field picks up on many aspects of Maxwell’s, but yet has a character all its own. No one could express this better than Boltzmann himself in a quote describing Maxwell’s achievements using a musical metaphor:

“Just as the musician recognizes Mozart, Beethoven, Schubert in the very first measures, so the mathematician can differentiate between his Cauchy, Gauss, Jacobi,

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<sup>16</sup>Idem: “The Second Law of Thermodynamics.” In: Boltzmann 1974, pp. 13–32, p. 31.

<sup>17</sup>Idem: “On the Principles of Mechanics.” In: Boltzmann 1974, pp. 139f.

<sup>18</sup>Ibid., pp. 146f.

<sup>19</sup>Idem: “On the Indispensability of Atomism in Natural Science.” In: Boltzmann 1974, pp. 41–53, p. 46.

Helmholtz after a few pages. The highest external elegance, with conclusions occasionally supported by a somewhat weak skeleton, characterizes the French; the greatest dramatic force, the English, above all Maxwell. Is there anyone who does not know his dynamic gas theory? – First it majestically develops the variations of velocity, then from one side the equations of states set in, from the other the equations of motion; the chaos of the formulas rocks ever higher; suddenly the four words sound, 'Put  $n = 5$ .' The evil demon  $V$  disappears, just as in music a wild figure in the bass line burrowing below it all is suddenly silenced; as if by a stroke of magic, all that had appeared uncontrollable falls into place. There is no time to say why this or that substitution is made; anyone who does not feel the reasons lays the book aside; Maxwell is no program musician who has to set an explanation over the notes. Obediently the formulas now play out result after result, until, as a surprising conclusive effect, the thermal equilibrium of a heavy gas is obtained and the curtain falls.”<sup>20</sup>

But what does kinetic gas theory deal with? For one, naturally, it is about the attempt to create a connection between the mechanical properties of the microscopic components of a gas, i.e., its molecules, and its thermal behaviour; but then, of course, it also concerns the fundamental connection between mechanics and thermodynamics as conceptually autonomous subdisciplines of physics, which were, in this sense, just becoming established in the mid-nineteenth century.

It is one of the essential insights of thermodynamics that while there is no restriction to transforming work into heat, heat can be transformed into work only to a limited degree. In the formulation by Clausius of 1850, the “second fundamental law of thermodynamics” states that it is impossible to transfer heat from a cold body to a warm one without performing work. Useful energy has, so to speak, a natural tendency to pass into useless heat, i.e., into a low-quality kind of energy. This insight can be subsumed accurately using the concept of entropy, which describes the quality of energy, and the second fundamental law of thermodynamics. For entropy increases to the same degree at which a system loses its capacity to work through irreversible processes. The second fundamental law thus expresses a one-sidedness in the processes of our world and, as such, a temporal direction as well.

In 1866 Boltzmann began his studies about the relation between mechanics and thermodynamics with the attempt to establish a direct connection between the second law and the mechanical principle of least action. However, picking up on Maxwell, he soon discovered that such a connection between mechanics and thermodynamics can be established successfully only if one also integrates the statistical behaviour of the microscopic components of a body, i.e., for instance, the statistical behaviour of the molecules of a gas.

Following Maxwell, Boltzmann was the first to determine with complete universality the ratio of molecules or atoms with a certain energy, by advancing what is known today as the “Maxwell–Boltzmann distribution.”

In 1877 he succeeded in establishing a connection between the thermodynamic entropy of a macroscopic physical system and the number of microscopic states which

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<sup>20</sup>Idem: “Gustav Robert Kirchhoff.” In: Boltzmann 1925, pp. 51–75, p. 73.

correspond to the macroscopic state. In so doing, Boltzmann found a relation between entropy, which, as mentioned above, characterizes the one-sidedness of the macro-world, and the probability of a state that makes out this one-sidedness from the perspective of the micro-world, and which results from the number of microscopic states that correspond to it. He interpreted entropy as a measure of the disorder of a system and attempted to show that isolated systems tend towards a state of maximum disorder.

Even earlier, back in 1872 – again picking up on Maxwell – he had made another attempt to connect thermodynamic entropy with the mechanical properties of the microscopic components of a physical system. In his famous  $H$ -theorem he established that a quantity  $H$ , which depends on the distribution of the velocities of the molecules of a gas, decreases until the distribution of velocities takes on its equilibrium value, which is determined by the Maxwell–Boltzmann distribution. The quantity  $H$  thus corresponds to the negative of thermodynamic entropy. With this Boltzmann appeared to have succeeded in deriving the essence of the second law of thermodynamics from Newtonian laws: entropy increases when the quantity  $H$  decreases. In this manner he also generalized the concept of entropy to conditions of non-equilibrium.

In the same famous paper of 1872 – also picking up on Maxwell – he created the essential prerequisites for understanding the transport properties of a gas, like its diffusion, viscosity and heat conductivity. Even today, the Boltzmann equation for transport processes plays a key role in the study of transport phenomena in liquids, plasmas and neutrons.

But in addition to his work on statistical physics, Boltzmann also made essential contributions to many other areas of physics. In electrodynamics, too, he picked up on Maxwell and contributed significantly to the propagation and acceptance of his work on the European continent. Boltzmann further made independent contributions to electrodynamics. For instance, in the same year of 1872 he published an experimental confirmation of Maxwell's claim that the optical refraction index for non-conductive bodies and gases is the geometric mean of the dielectricity constant and magnetic permeability. Thus he provided an empirical confirmation of the connection Maxwell asserted between optics and electromagnetism.

Boltzmann also developed a theory of elastic effects in which the tension of a body depended on its deformation history. And he succeeded in finding a theoretical derivation of what is known today as the Stefan–Boltzmann law, according to which the energy of radiation in thermal equilibrium is proportional to the fourth power of the temperature – and did so on the basis of the second law of thermodynamics and Maxwell's electromagnetic theory. As if all of this and much else that Boltzmann achieved scientifically were still not enough, a number of his admirers also make him out to be a trailblazer of quantum theory, even of the special and general theories of relativity. So the eighth volume of the complete edition of his works concludes with the almost mystical sounding assertion, “In any case it is true that Boltzmann, as in flash photograph, took a preliminary glance at the edifice erected by Einstein.”<sup>21</sup>

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<sup>21</sup>Motz, Hans: “Did the Germ of General Relativity Come from Boltzmann?” In: *Ludwig Boltzmann: Ausgewählte Abhandlungen*, R. Sexl and J. Blackmore (eds.), Vol. 8 of the complete edition. Graz: Akademische Druck- und Verlagsanstalt, pp. 354–360, p. 360.

On the one hand, such assessments may well appear somewhat exaggerated beyond the context of commemorative ceremonies and publications. After all, Boltzmann also wrote about aviation, radio waves and life on other planets. Thus one passage reads, “I hold it probable that on Mars oceans, continents, snow exist; that planets similar to the Earth rotate around other fixed stars; that among these probably one or the other is populated by beings that are similar to us in some aspects, but different in others.”<sup>22</sup> Nevertheless, Boltzmann is not generally counted among the fathers of the airplane, radio, or the SETI program.

On the other hand, the multitude of Boltzmann’s scientific insights that found a direct or indirect continuation in today’s physics suggests a view that sees in Boltzmann not the representative of a lost world, but rather a kind of contemporary who seems surprisingly modern to us in many ways, even as regards – in view of a prominent contemporary Viennese physicist – his lush beard growth.

## Boltzmann and scientific progress

**The compatibility of the two perspectives.** Are these two different perspectives compatible with each other and what exactly do they imply for the historiography of modern physics? Are they simply the perspectives of the historian of science and the modern physicist that can co-exist, each with its own *déformation professionnelle*?

I believe that the question as to the compatibility of these perspectives conceals a much deeper question, namely one about the character of scientific progress. As a physicist one tends to look at scientific progress as a more or less constant expansion of our knowledge. Since Thomas Kuhn at the latest, the historian of science is, however, prepared for the existence of scientific revolutions that make sweeping changes to the conceptual frameworks within which we conceive of the world and attempt to resolve its problems.

Although it is difficult to recognize at first glance how these two perspectives fit together, they both have their entitlement, but each of them also leaves questions open. If, say, scientific progress is a constant growth of findings, how does it happen that fundamental concepts like those of space, time, matter and radiation can be altered in the course of the history of science, and especially in the transition from classical to modern physics?

And if there really is such a thing as scientific revolutions, which, as Kuhn asserts, overthrow old paradigms and establish new paradigms of scientific understanding of the world, then this poses the question as to what actually happens with the knowledge handed down during such a rupture, and, above all, where the new paradigms ultimately come from and how they emerge.

And finally: how does it happen that the new, revolutionary theories of modern physics emerged at precisely that time when classical physics appeared to be approaching its conclusion?

Although it may seem surprising in view of Boltzmann’s conservative attitude, he

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<sup>22</sup>Idem: “Ein Wort der Mathematik an die Energetik,” l.c., p. 133.

himself left no doubt as to his conviction that there are scientific revolutions: “The layman may imagine the matter such that new findings are added over and again to the basic ideas and root causes of phenomena that already have been discovered, and thus nature is recognized more and more in a continuous development. Yet this idea is erroneous; the development of theoretical physics has always taken place by leaps and bounds.”<sup>23</sup>

May we thus conclude that Boltzmann was not only the progenitor of the theory of relativity, but also the actual father of the Kuhnian theory of the structure of scientific revolutions?

**Towards a historical theory of scientific revolutions.** In the following, I will indicate that there is a conception of scientific revolutions that not only provides an answer to the questions about the compatibility of continuity and upheaval posed above, but also reconciles the two perspectives on Boltzmann as the man of yesterday and the man of today.

This conception further allows us to understand why classical physics fell into crisis so close to its accomplishment – and also in what sense this very crisis was able to become the point of departure for modern physics.

The revolutions of modern physics at the start of the twentieth century, in particular the revolutions of relativity and quantum physics, can be understood to be further developing and breaking through the mechanistic worldview at the same time. This becomes clear when we recall that it was precisely the most basic concepts of mechanics that experienced an essential modification through these revolutions, that is, the concepts of space, time and matter, in the words of the famous book title by Hermann Weyl.

However, additional areas of knowledge besides mechanics had crystallized in the classical physics of the nineteenth century, in which a more or less autonomous conceptual foundation had become established, including electrodynamics with concepts like field, current and charge, and thermodynamics with concepts like temperature and entropy.

Yet mechanics, with its concepts of space, time and matter, still provided the common framework of all physical knowledge. Beyond this, it still appeared possible to trace thermal and electromagnetic phenomena back to a mechanistic foundation using mechanical models and invisible mechanisms. In this way heat could be interpreted as a movement of atoms, and electromagnetic fields as states of an all-permeating aether.

Yet it would be wrong to see these explanations under the aspect of a mere dogmatic reductionism that traces everything back to mechanics. For these mechanical models also had an entirely different function from that of describing electromagnetic and thermodynamic phenomena in the framework of a mechanistic worldview. They also made it possible to relate the conceptual foundations of the various sub-areas of classical physics to each other, and to test them for mutual compatibility.

This happened particularly on the basis of the borderline problems that arose between these sub-areas, presenting highly concrete physical challenges, such as the prob-

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<sup>23</sup> Idem: “Josef Stefan”. Lecture held at the unveiling of the Stefan-Memorial on 8 December 1895. In: Boltzmann 1925, pp. 92–103, p. 94.

lem of the electrodynamics of moving bodies, for instance, quite obviously a problem at the borderline between electrodynamics and the theory of motion, i.e. mechanics. How do electrodynamic phenomena like light behave in such a moving reference system? Does the speed of light change in a moving reference system? Can a light beam be overtaken? These were the questions posed by young Einstein, thus connecting electrodynamic statements about light to the relativity principle of mechanics.

As long as one proceeds from the existence of an invisible mechanism like the aether as the carrier of light waves, however, it is difficult to find a satisfactory answer to these questions. In his famous paper of 1905 on the electrodynamics of moving bodies, Einstein therefore removed this invisible mechanism, introducing in its place the new concepts of space and time of the special theory of relativity.

But what does all this have to do with Boltzmann? Well, if one looks only at an *annus mirabilis* like the year 1905, it is easy to forget that Einstein's ingenious solution to the problems of the electrodynamics of moving bodies would have been inconceivable had not the possibilities of the mechanistic worldview, and in this case the possibilities of the concept of aether, previously been exhausted to depletion.

Although Boltzmann also contributed to electrodynamics, especially, as mentioned above, by making Maxwell's theory known on the Continent, in this case the greatest credit is due to the Dutch physicist Hendrik Antoon Lorentz. Einstein's theory of relativity of 1905 is in fact basically a mere reinterpretation of Lorentz's theory, just without the mechanical aether. So much to the borderline problem of the electrodynamics of moving bodies; the source of the relativity revolution.

In a similar manner, the problem of thermal radiation, a problem on the borderline between radiation theory – i.e., electrodynamics – and the theory of heat, became the source of the quantum revolution, and the borderline problems between mechanics and thermodynamics the point of departure for modern statistical physics.

To the understanding of these borderline problems Boltzmann provided what were probably his most important contributions, above all by plumbing the borders of the mechanistic worldview and revealing its internal tensions, which were to become the driving forces of the scientific revolutions of modern physics.

In this manner the new emerged amidst the old, or, in other words, the great innovations of modern physics were ultimately nothing other than the result of an occasionally radical, but occasionally only minimal reorganization of the knowledge accumulated by classical physics.

That is the background as to why questions like whether the theory of relativity owes more to Lorentz or Einstein, whether the quantum revolution begins with Planck or Einstein, or the extent to which the statistical mechanics of a Josiah Willard Gibbs or Einstein reach significantly beyond Boltzmann, are ultimately moot.

While miraculous years are often at the centre of attention, they are inconceivable without the tedious work of extending an existing edifice of knowledge, particularly with a view to the cracks in the building, which typically become more evident during such a construction project, so that ultimately nothing remains but to erect a new edifice from the old building's ruins.

## Boltzmann as the trailblazer of a revolution

Against the background of such a conception of scientific revolutions which enables the dimensions of continuity and rupture to be reconciled, it is now possible to understand the sense in which Boltzmann was one of the greatest trailblazers of the scientific revolutions at the beginning of the twentieth century. He did indeed create essential prerequisites for the solution of the borderline problems of classical physics, and through the very elaboration of the inner tensions of classical physics, contributed to surmounting them.

But what exactly were these tensions? They are manifested primarily in the idea of invisible mechanisms upon which the theories of classical physics were based, that is, those of the aether and of the atoms.

**The aether.** As mentioned earlier, Boltzmann was one of the essential promoters of Maxwellian electrodynamics, which was based on the concept of the aether. Through Maxwell's theory the optical aether, as the medium for propagating light waves, was conflated with the electromagnetic aether as the carrier of electromagnetic fields. As such it became, however, increasingly difficult to develop a consistent mechanical model of the aether. The aether suffered, so to speak, from a Figaro problem: Like the Figaro of Beaumarchais, Mozart and Rossini, also the classical aether was overwhelmed by an ever larger number of demands.

Nevertheless, Boltzmann occupied himself intensively with the possibility of a way to present electrodynamic processes mechanically, and worked out a lecture on Maxwell's electrodynamics, published as a book in 1891 and 1893, in which this mechanical presentability plays a key role.<sup>24</sup>

On the one hand, this lecture used the theoretical instruments of mechanics, especially the Lagrange formalism and the principle of action. On the other hand, he quite concretely constructed mechanical models of electrodynamic processes, such as the elaborate gearing mechanism that was supposed to illustrate the inductive coupling of two electric circuits. However, he did not succeed in constructing a consistent mechanism of aether. But it was precisely such failures that ultimately prepared the ground for its supersession.

Boltzmann himself regarded the aether problem as a key issue. Thus he asked in one of his texts, with a view to the future development of physics, “Will the mechanist view of nature one day win the decisive battle for the discovery of a simple mechanical picture of the luminous aether [...]?”<sup>25</sup>

Ultimately, he also regarded contemporary attempts to trace mechanics back in the opposite direction to electromagnetism as an alternative pathway towards a conceptual unification of physics within the framework of what he still considered to be basically a mechanical worldview. From his perspective these attempts could not escape the

<sup>24</sup>Boltzmann, Ludwig. 1891/93. *Vorlesungen über Maxwells Theorie der Elektrizität und des Lichts.* 2 vols. Leipzig: Johann Ambrosius Barth.

<sup>25</sup>Idem: “On the Development of the Methods of Theoretical Physics in Recent Times.” In: Boltzmann 1974, p. 77–100, p. 100.

question of the nature of the aether, “The best known law of mechanics is the principle of inertia. Every high school boy is familiar with it today – I speak of course only of inertia in the physical sense. Until recently the law of inertia has been regarded as the foremost fundamental law of nature, itself inexplicable but essential for explaining any phenomena. However it is a consequence of Maxwell’s equations for electromagnetism, that a moving electrical particle without any mass or inertia of its own must move, by the mere action of the surrounding aether, just as though it had inertial mass. [...] Whereas previously one wanted to explain all phenomena in terms of the action of mechanisms, now it is the aether that is a mechanism, quite obscure in itself of course, that is to explain the action of all other mechanisms. It was no longer a question of explaining everything mechanically, but of finding a mechanism to explain all mechanisms.”<sup>26</sup>

But aside from speculations about the nature of the aether, Boltzmann also ultimately contributed – albeit rather indirectly – to the supersession of the aether through quite concrete work, for instance, through the above-mentioned theoretical derivation of the Stefan–Boltzmann law, according to which the energy of radiation is proportional to the fourth power of the temperature. This law concerns the problem of thermal radiation and thus a problem on the borderline between electrodynamics and thermodynamics. In fact, Boltzmann’s derivation of this law is actually based on the second law of thermodynamics and Maxwell’s electromagnetic theory. Later Einstein was able to use the Stefan–Boltzmann law and his famous formula for the fluctuations of a physical system, which also picks up on Boltzmann’s statistical methods, to show that Maxwell’s theory does not predict the fluctuations that would be expected according to the Stefan–Boltzmann law.<sup>27</sup>

In other words, the combination of different elements of classical physics yielded a result that could not be reconciled with classical physics. It was not only difficult to design a mechanical model of the aether, it was also difficult to bring the aether into accord with the knowledge of thermodynamics. But such a verification could only succeed at all because Boltzmann had provided the necessary tools.

**Atoms.** The main contribution by Boltzmann to the transformation of classical physics into modern physics was concerned with the problems on the borderline between mechanics and thermodynamics, making him one of the founders of modern statistical physics.

Today the statistical properties of physical systems are part of the basic elements of physics. Statements about statistical behaviour essentially characterize the behaviour of physical systems. Just think of the Bose–Einstein statistics, for instance, which proceeds from the assumption that individual particles cannot be distinguished, so that the commutation of particles does not yield a new macroscopic state. From this statement, fundamental quantum properties of such systems emerge, as in the case of light, for instance, the possibility of the laser principle.

<sup>26</sup>Idem: “On the Principles of Mechanics.” In: Boltzmann 1974, pp. 149f.

<sup>27</sup>Rynasiewicz, Robert and Jürgen Renn. 2006. “The Turning Point for Einstein’s *Annus Mirabilis*.” *Studies in History and Philosophy of Modern Physics* 37, pp. 5–35.

In Boltzmann's day, however, statistical properties were still determined by translating macroscopic experiences into the microcosm of atoms, such as the distinguishability of particles. But precisely the explicitness of the assumptions with which Boltzmann described such behaviour later made it possible to consider other, non-classic assumptions as well, like the above-mentioned Bose–Einstein statistics.

The generalization potential of Boltzmann's insights into the role of statistics in physics becomes especially clear on the basis of the above-mentioned relation he established between entropy and the probability of a microscopic state. Boltzmann used this relation to infer the known thermodynamic properties of a system from plausible assumptions about microscopic states.

Einstein, in contrast, later used this relation to infer unknown microscopic properties from the thermodynamic properties of a system, postulating, for instance, that under certain circumstances thermal radiation would behave like a gas of light particles. Planck had made use of Boltzmann's statistical methods before to derive his famous radiation law. In this manner Boltzmann's statistical methods thus became an essential instrument of the quantum revolution.

With similarly surprising consequences, the methods developed by Boltzmann were used to interpret Brownian movement, the irregular motion of particles suspended in liquids. This phenomenon had long remained a riddle, but Einstein and Marian von Smoluchowski were able to interpret it as the result of the interaction of the suspended particles with the thermal movement of the molecules of the liquid. Above all it was this interpretation that helped the long-controversial atomism to its breakthrough, for now such suspended particles could be conceived of, so to speak, as a sort of atom visible under the microscope. As such the famous reply by Mach to the question as to the existence of atoms, "have you seen any?" could finally be answered in the affirmative. For the suspended particles, with their Brownian movement, apparently behaved just as if they were large atoms that had happened into the range of visibility.

**The tensions of classical physics.** The foundation for the revolutionary insights related above were results Boltzmann had obtained in confronting the internal tensions of classical physics. This confrontation was practically inevitable, emerging from his central interest in the question as to the extent to which those challenging scientific objects, which we can conceive as thermodynamic systems, still can be understood in the framework of mechanics. He was less interested in individual aspects like relaxation times, the observability of fluctuations and the like, but rather in this fundamental question. In order to find satisfactory answers, he was even willing to expand his conception of mechanics, in particular by introducing statistical elements like the idea of stochastic processes. His point of departure within mechanics was the Hamiltonian formulation rather than the Newtonian version, because he was concerned with the behaviour of a system as a whole. And the point of departure of his statistical thought was the conception of the objective irrelevance of certain information, not that of a subjective ignorance.

With the  $H$ -theorem mentioned above, Boltzmann initially appeared to have more or less achieved his goal of a mechanical explanation of the second law of thermodynamics.

Yet the  $H$ -theorem raised new issues in the borderline area between mechanics and thermodynamics. Thus in 1876, following Lord Kelvin, Joseph Loschmidt objected that one need only imagine that all velocities of the molecules in a gas had to be inverted to arrive at the opposite of the predication of the  $H$ -theorem. Indeed, such an inversion is permissible in principle, for the laws of mechanics permit an inversion of the temporal direction. But if the  $H$ -function decreases for the original system, then it must increase for the system with an inverted temporal direction. Therefore it appeared as if the  $H$ -theorem could not hold and, in any case, could not provide any mechanical explanation of thermodynamics.

In his response Boltzmann pointed out that this conclusion can be avoided if one also considers the initial conditions of a physical system, and conceives of the  $H$ -theorem as a statement that is essentially statistical. For while each individual, uniform distribution of the molecules is just as improbable as every other distribution, however non-uniform it may be, there are simply unbelievably more initial conditions that lead to a uniform distribution than initial conditions that lead to a non-uniform distribution. Ultimately, however, this yields that for a macroscopic initial condition that is not a state of equilibrium, and for a finite time in which the system develops, the number of compatible micro-states in which  $H$  decreases is much greater than the number of the micro-states in which  $H$  increases.

But with this, the problem of reconciling the reversibility of the temporal direction of mechanical processes with the non-reversibility in thermodynamics was by no means resolved completely. For the statement that there is a much greater number of uniform states does not also mean that one and the same system exists in a uniform state over a longer period of time. This is true only if one can show that what is known as the “ergodic hypothesis” holds, that is, the claim that the system spends exactly the same amount of time in each of its theoretically possible micro-states. On the other hand, however, one can also make specific assumptions about the dynamics of the interaction among the microscopic components of a system which determine its temporal development. Statistical physics is indeed still concerned with such fundamental questions today.

My point here is simply to demonstrate that Boltzmann’s occupation with the problems on the borderline between mechanics and thermodynamics was the motor that drove him to develop ever more sophisticated tools of statistical physics, which ultimately became the key instruments of modern physics. Precisely because of their high degree of independence from specific dynamic conceptions, they made it possible for him to pave the way for quantum theory as well.

**Boltzmann’s vision.** In closing, let us return again to Boltzmann’s perspectives and in particular to the question of his expectations for the future. His ideas of future technological developments turned out to be extraordinarily realistic. As early as 1894 he was certain that the future belonged to the airplane: “Thus it appears that the aeroplane propelled by the propeller is the theoretically most promising mechanism and the only one which has already actually lifted off both in the form of smaller models and in a larger version. It is unbelievable how simple and natural every result seems once it has been found, and how difficult, as long as the path leading to it remains unknown. As

such, even manual labourers will one day be able to steer the airplane; but only a genius of the first rank can invent it.”<sup>28</sup>

Apparently, in this vision of the future Boltzmann was absolutely right. But it is rather dubious that he hit on the right prediction for the future of human biology as well. With reference to experiments he had become familiar with in America, he wrote, “Löb [...] demonstrated, that [...] the same effects which are otherwise induced on eggs only by male semen, can be exerted by completely lifeless acids. [...] An emancipation of women far beyond what today’s women’s rights activists could ever dream. [...] It will not be long before we find out which combination produces boys, and which girls, and since the former are completely superfluous, only a few specimens will be generated for the zoological gardens.”<sup>29</sup>

He saw science as in the process of rapid acceleration: “Especially the development of natural science in recent times resembles rather that of a modern American town which in a few decades grows from a village into a city of millions.”<sup>30</sup>

Boltzmann expressed his concern about the fact that in the face of such explosions of knowledge it was easy to be overwhelmed and lose track of the perspective on the whole of science. “The consequence of this vast and rapidly growing extent of our positive knowledge was a division of labour in science right down to the minutest detail, almost reminiscent of a modern factory where one person does nothing but measure carbon filaments, while another cuts them, a third welds them in and so on. Such a division of labour certainly helps greatly to promote rapid progress in science and is indeed indispensable for it; but just as certainly it harbours great dangers. For we lose the overview of the whole, required for any mental activity aiming at discovering something essentially new or even just essentially new combinations of old ideas.”<sup>31</sup>

As far as the imminent revolutions in physics are concerned, in the end he must have sensed their advent. Thus, with a view to the discoveries by Hertz, Röntgen, Rowland and Hall, he remarked, “Most of the quite novel phenomena here described are so far known only in their basic features. Exploring them as to detail and as to their relations to each other and to the rest of all known phenomena, their embedding into the mechanical physical loom, to use somewhat exaggerated language, all this will open up a future field of work of seemingly boundless extent. The copious practical results achieved from the very start (X-ray photography, wireless telegraphy, radiotherapy) allow us to imagine the practical gain that detailed research will afford, which is ordinarily required before any fruitful results emerge. Theory, however, has been shaken from its complacency in which it thought it had already recognised everything, nor has it been possible yet to gather the new phenomena into as uniform a theoretical structure as the old theory had been. Everything remains rather in a state of indecision and ferment.”<sup>32</sup>

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<sup>28</sup>Boltzmann, Ludwig. “Über Luftschiffahrt.” In: Boltzmann 1925, pp. 81–91, p. 90.

<sup>29</sup>Idem: “Reise eines deutschen Professors ins Eldorado.” In: Boltzmann 1925, l.c. p. 427.

<sup>30</sup>Idem: “On the Development of the Methods of Theoretical Physics in Recent Times.” In: Boltzmann 1974, p. 77–100, p. 77.

<sup>31</sup>Ibid., p. 77f.

<sup>32</sup>Ibid., p. 87f.

There is no question that he was open to these developments, and, indeed, had already clearly seen the key role of spectra for a future atomic physics on new foundations, like the one then founded by Niels Bohr, “Only the solution of the most obvious task, to receive from the nature of the spectra themselves conclusions about the nature of the oscillating molecules, refused to find success; yet here, too, a beginning has been made through the discovery of the extremely wonderful laws of periodicity of the spectral lines, and the historian of the future will certainly be able to tell more details.”<sup>33</sup>

Of course, he believed that it would be possible to solve even this puzzle using atomism, but nevertheless he was open for a new atomism, “As regards ideas about the nature of the molecules it will however be necessary to leave the widest possible room for manoeuvre [...] for molecules do not behave like elastic bodies except for the simplest gases and even for them not at very high temperatures and only as to their collisions; about their more detailed constitution which is bound to be very complicated we have as yet no indications, rather we shall have to try to find them.”<sup>34</sup>

Boltzmann saw atomism in a similar way as young Einstein later did, as a kind of interdisciplinary undertaking that represented a developable foundation for interpreting the knowledge of the various sub-areas of classical physics and chemistry: “To get closer to this last goal [proposal of a comprehensive picture of nature], current atomism does indeed seek to reconcile the foundations of the various phenomenological atomisms by arbitrarily completing and altering the properties of the atoms required for the various factual domains in such a way that they may serve for representing many domains at the same time.”<sup>35</sup>

In closing this brief excursion on Boltzmann’s expectations for the future, let us look at his own *caveat*: “It is especially attractive to follow up a historical account with a look at scientific developments in a future that, in view of the short span of human life, none of us can experience. As to that let me confess at once that all I have to say will be negative. I will not be so rash as to lift the veil that conceals the future, but I will offer reasons that should be apt to warn us against certain hasty conclusions as regards future scientific developments.”<sup>36</sup>

**Conclusion.** In this very caution, connected with the warning against false prophets, lies one of Boltzmann’s greatest strengths. One of the concerns of this paper is to honour Boltzmann as someone who stood as a visionary and yet was filled with humility at the end of an era. He resisted the false prophets of the future, thus keeping the door open for the right ones. He conceived of physics as part of a confrontation about worldviews without ever succumbing to any dogmatism. His tragic fate, however, should also be a warning to us, because he was in error precisely where he supposed he was at a conclusion, without knowing that a new beginning would follow. In so doing, he himself had pronounced the best comfort about our inability to see into the future:

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<sup>33</sup>Idem: “Gustav Robert Kirchhoff,” In: Boltzmann 1925, pp. 51–75, pp. 63, 65.

<sup>34</sup>Idem: “On the Development of the Methods of Theoretical Physics in Recent Times.” In: Boltzmann 1974, p. 77–100, p. 99.

<sup>35</sup>Idem: “On the Indispensability of Atomism in Natural Science.” In: Boltzmann 1974, pp. 41–53, p. 46.

<sup>36</sup>Idem: “On the Development of the Methods of Theoretical Physics in Recent Times.” In: Boltzmann 1974, p. 79.

“Interesting questions indeed! One almost regrets having to die long before they are decided. How immoderate we mortals are! Delight in watching the fluctuations of the contest is our true lot. For the rest, it is better to work on what lies close to hand rather than rack one’s brains about such remote questions.”<sup>37</sup>

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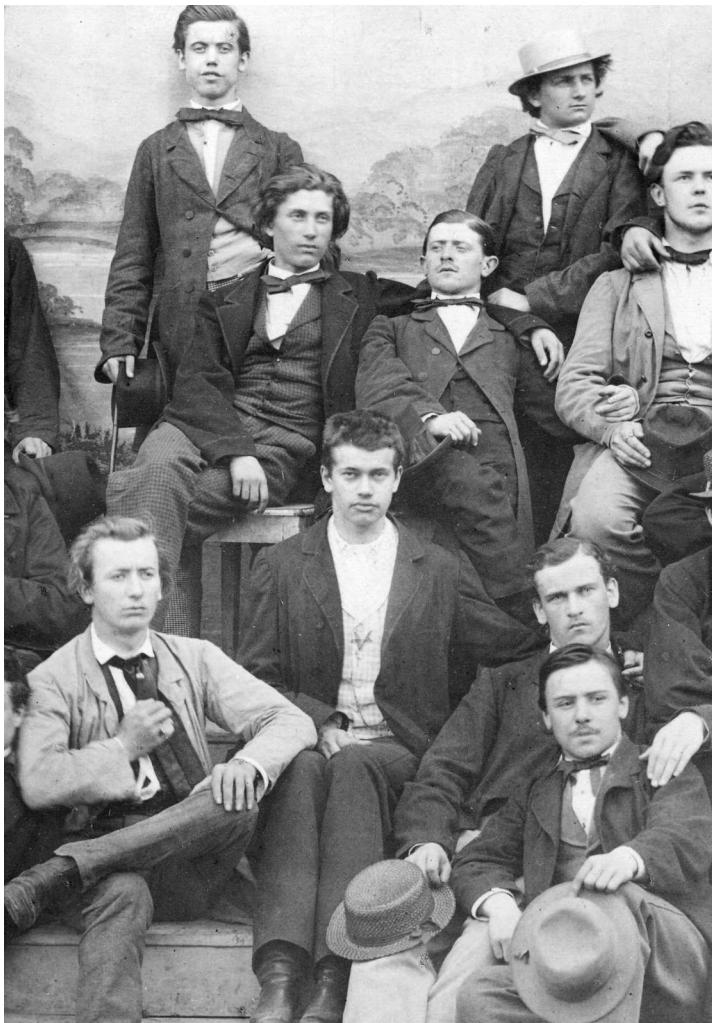
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Ludwig Boltzmann (center) with fellow students after the Matura in Linz 1863  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)

# What if Boltzmann had known about quantum mechanics

Elliott H. Lieb

## Introduction

It was an honor to be asked to speak at the Symposium on “Boltzmann’s Legacy”. The nineteenth century saw a great flowering of science, especially physics, and several far reaching conceptual advances were made that forever changed our view of the world and its constituents. Among these it is difficult to think of a breakthrough greater than Boltzmann’s, whose work allowed us to understand how macroscopic physics arises out of many-body dynamics on the scale of atoms. Many physicists believe that the essence of physics is understanding the detailed interactions between particles, and the importance of a theory is often gauged by how high the energy is of the particles and fields being described. But Boltzmann’s branch of physics goes in another direction. He describes the complexity generated by multiple interactions among particles without focusing too strongly on the details of the interactions themselves.

We praise and honor the memory of a man who had the courage and conviction to go well outside the paradigm of his day. There have been some changes, however, to the details of Boltzmann’s picture in the 100 years since his death, and it is these that I wanted to talk about. For example, it turned out that one had to go to subatomic scales, to electrons and nuclei, to fully understand our ordinary world [3]. Others at the symposium elegantly recalled Boltzmann’s ideas, but I wanted to emphasize some necessary perturbations of the original picture that, I feel, are not sufficiently prominent in the lessons we teach our students. One of these is quantum mechanics, which usually does not play a prominent role in most statistical mechanics textbooks. There are exceptions to this rule, such as [1] or [6], but even the author of [6] felt it necessary to warn the reader (in the preface) that his book is radical.

Boltzmann’s main idea can be summarized in the following way: *The macroscopic properties of matter, perhaps even down to the mesoscopic level* (a concept presumably not clearly articulated in Boltzmann’s day as it is in ours) *can be explained, or accounted for, by applying probability theory to local, deterministic mechanics.* In this way, one could ‘explain’ the second law of thermodynamics. For example, Gibbs wrote (quoted in [6], p. 105):

*“The laws of thermodynamics may easily be obtained from the principles of statistical mechanics, of which they are the incomplete expression.”*

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Based on a talk given at the Symposium “Boltzmann’s Legacy”, in commemoration of Ludwig Boltzmann’s death on September 5, 1906, at the Erwin Schrödinger Institute, June 7, 2006.

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While more than a century of devoted effort has made the laws of thermodynamics plausible consequences of mechanical principles, it has neither been “easy” nor has the program been fully accomplished. Several speakers at the symposium told us about the excellent progress that has been made and about the ongoing efforts to complete the program. Boltzmann’s decisive and lasting insight was that *statistical ensembles* would lead to the Clausius inequality, but one must go further and ask about the connection with deterministic mechanics.

It is certainly true that Boltzmann’s concept that thermodynamic entropy of a macroscopic system at energy  $E$  is proportional to the logarithm of the area of the surface in phase space corresponding to the energy  $E$  is a major one. For a system in which the energy surface is discrete this gives us the famous formula

$$S = k_B \log W, \quad (1)$$

where  $W$  is the number of states of a given energy and  $k_B$  is Boltzmann’s constant. For a more general state, (in equilibrium at constant energy or not, continuous or discrete) one can replace (1) by a more general formula

$$S = -k_B \int_{\text{phase space}} \varrho \log \varrho, \quad (2)$$

where  $\varrho$  is the probability density in phase space.

Formula (1), written on Boltzmann’s gravestone, or (2), works very well in practice and has definite predictive value. For instance it shows, effortlessly, that removing a constraint increases the entropy  $S$ . But the derivation of this formula from deterministic mechanics is not a closed chapter. (For examples in which removal of a constraint in a simple physical system does not lead to an increase in entropy, or does not lead to a definite, predictable entropy increase, or does not lead to the “maximal possible” entropy increase see the “piston problem” [9].)

Another problem, to which we shall return in the next section, concerns the inclusion of quantum mechanics, which we know to be of critical importance in many cases. One replaces (2) with

$$S = -k_B \text{Trace}(\varrho \log \varrho) \quad (3)$$

where  $\varrho$  is a quantum-mechanical density matrix. This formula, essentially due to von Neumann, is largely justified by analogy with the classical theory, but its derivation from quantum mechanics is less secure.

Much remains to be done if a derivation of the laws of thermodynamics is to be found that is free of physical assumptions and uncontrolled mathematical approximations. Even a simple plausible mechanical model to illustrate unambiguously the seemingly simpler, and ‘obvious’ Fourier law of heat conduction (i.e., that the temperature in a thermally conducting rod changes linearly as one moves from the hot end to the cold end) has yet to be found, despite a diligent search for one [2].

To questions of these kinds one may add others.

- What, precisely, are the physical laws of thermodynamics that one wants to derive from statistical mechanics. In particular, what, exactly, is the meaning of the second law that one wants to derive from dynamical principles?

- What is the underlying mechanics from which they are to be derived?
- From the epistemological perspective, *how unique is the theory?* That is to say, can the same physical conclusions be derived from an alternative theory? Is Boltzmann's theory falsifiable?

I will not have much to say about the third question, but it is worth asking and it is not completely disconnected from the first question. To a physicist a question like this is a waste of mental energy because we do know that atoms exist, so why bother with alternatives. The point is that the deduction of the second law from a certain mechanical picture may not be as impressive as thought at first. If the second law follows from other (wrong, but not “unphysical”) assumptions then the implication is that we need not consider the second law to be astonishing, but rather that it is hard to avoid.

The following quotation [5] from L. Kadanoff illustrates the content of the third question

*“Boltzmann was right about atoms but utterly wrong in believing that atoms provided a necessary basis for thermodynamics. The second law does not require atoms. Thermodynamics would be equally correct if the basic constituents of the world were atoms, or quantum fields, or even strings.”*

While this may not be completely fair to Boltzmann, it is true that the laws of thermodynamics do not directly tell us about atoms. The macroscopic laws of thermodynamics, by themselves, do not reveal properties of atoms, for otherwise the argument in Boltzmann's time about the existence of atoms would not have taken so long to resolve. (Fluctuations of macroscopic quantities are another matter, however; they do reveal properties of atoms and this was crucially important in resolving the debate.)

The second law in the sense of the existence of entropy is very general – which is what Giles [4], Yngvason, and I [10], and Carathéodory in 1909 have proposed and which I will discuss as an example of the first question above in Section 2.

If atoms are not necessary for the second law of thermodynamics, what *is* necessary? I will come back to this in Section 3, after discussing the second question with several examples.

## 1 The importance of quantum mechanics

The basic dynamics governing the motion of atoms, as well as their internal degrees of freedom, is quantum mechanics. It can modify the picture based on classical mechanics and its predictions substantially, even at ordinary temperatures, depending on the question that is being addressed.

**Example 1.** The mean free path of a nitrogen molecule in air at room temperature and pressure is about 100 times its radius. During the flight of a molecule from one collision to the next the Heisenberg uncertainty,  $\Delta \vec{p} \Delta \vec{x} > \hbar$ , in the velocity component perpendicular to the main velocity component is significant. Effectively, the trajectory is

not a line but (very roughly speaking) a *cone*. (This can be modeled more accurately by using the Mehler kernel to solve the free-particle Schrödinger equation, but that is not important for this discussion.) My estimate of this effect, given the mass of a nitrogen molecule is that by the time a molecule reaches its next collision the uncertainty in the location of the collision point is of the order of the molecular radius. Even if this calculation is not completely accurate, the conclusion cannot be avoided that *after several collisions it is hard to see that the classical trajectory has much meaning*.

The intrusion of quantum mechanics makes the earlier, classical Poincaré–Löschermidt–Zermelo *recurrence paradoxes*, and similar matters such as time reversibility, less important. One may say that they are largely academic. It even makes discussions of the Stoßzahlansatz somewhat academic. It is not inconceivable that the smearing effect of quantum mechanics may well play a role in the problem of coincident points in the highly successful Boltzmann transport equation. In other words, the ‘noise’ caused by quantum mechanics may be a component of the derivation of the Euler and Navier–Stokes equations, but since I am not an expert in these matters I do not want to emphasize this point.

In any case, it may be useful to point out that quantum mechanics is not truly a theory that is invariant under time reversal. While it is true that Schrödinger’s equation is invariant under time reversal, there is the unpleasant notion of the “collapse of the wave function” that looms in the background. If one macroscopic system is brought (by accident or by an experimenter) into contact with another macroscopic system is this a measurement? And if it is, does the wave function change discontinuously? These effects are related to ‘*decoherence*’, but whatever their nature it implies an irreversibility that it might be well to take into account when considering ‘paradoxes’.

Although classical dynamical calculations of the motion of atoms often give results in good agreement with experiment, it is hard to see why this is so. One well known expert on statistical mechanics has described this unexpected good luck to me as “a miracle”. It has to be remembered, however, that the parameters in the classical modeling depend on the experiment being studied. Whether the results agree or not (and they certainly do not agree at low temperature) the fact is that:

*The paradigm of local determinism plus probability theory does not hold with infinite precision. Quantum-mechanical dynamics is not totally deterministic ab initio, although it may occasionally be well described by deterministic mechanics. It is also not truly time reversible because of decoherence and the postulates about the collapse of the wave function.*

In other words, the concepts of molecular ‘chaos’ and ‘sensitivity to initial conditions’ may not be the *sole* explanation for the success of statistical mechanics and probabilistic reasoning.

**Example 2.** We all know that quantum mechanics plus the Pauli exclusion principle is needed to account for the stability of ordinary matter [3]. The fact that matter does not collapse under the influence of attractive electrostatic forces is due solely to quantum mechanics. Nevertheless, we can use quantum mechanics to calculate ‘effective’ low

energy interactions among atoms using the Born–Oppenheimer approximation (e. g., Lennard–Jones potentials) and it has been shown that classical mechanics using these potential energy functions gives good answers.

There is, however, a caveat. Since the interaction of atoms is caused by electronic motion, and not simply by static potentials, this classical approximation cannot be completely accurate. There are velocity dependent effective interactions, at the very least. The Lennard–Jones potential is suitable for calculating the properties of dilute gases, but the *same* potential, with the *same* parameters can not yield the cohesive energy of solids accurately because the electronic states of the atoms are different in the two cases.

**Example 3.** Even at room temperature, some weird properties of quantum mechanics come to the fore. Notably, the Pauli exclusion principle, without which we cannot begin to understand many simple properties of solids. However, at high temperatures and moderate densities a classical description (with potentials determined from quantum mechanics) often works well (but note that quantum mechanics implies that *kinetic energy is not the same as temperature*, as Boltzmann had to assume). An example where classical mechanics and ensemble theory fails, even at room temperature, is the orbital diamagnetism of an electron gas; diamagnetism is completely absent classically (van Leeuwen’s theorem).

The reason that classical mechanics can be a good approximation to quantum mechanics for equilibrium situations has only slowly been really understood in the last half century; the semiclassical description of quantum mechanics is much better, on the average, than one could have expected. And in equilibrium situations we are, indeed, interested in averages.

**Example 4.** At low temperatures quantum effects are not only crucially important, they are determining. These effects are well known but often presented to students of statistical mechanics as exceptions. While it is true that many of their thermodynamic effects can be understood by substituting quantum traces for classical integrals, it ought to be emphasized, much more than it normally is, that twentieth century physics caused a major departure from Boltzmann’s physical picture. Several effects can be noted.

- Specific heats are suppressed relative to their classical values.
- Even low density gases, liquids and solids cannot be understood without understanding Bose–Einstein and Fermi–Dirac statistics (the Pauli exclusion principle). It hardly needs to be stressed that there is no classical analog to many properties of these gases and liquids. Superfluidity, superconductivity and Bose–Einstein condensation run completely counter to Boltzmann’s intuition that the world gets more and more chaotic as time progresses.
- Any reasonable *classical* theory of gases, using the Boltzmann density in phase space  $\varrho \sim \exp[-H/k_B T]$  will give an entropy that goes to negative infinity (instead of to zero or to a positive number) as the temperature  $T$  goes to

zero. For positive entropy we need quantum mechanics together with von Neumann's generalization to traces in Hilbert space of the '*operator density matrix*'  $\varrho \sim \exp[-H/k_B T]$ . Are we absolutely certain that this 'obvious' generalization is completely correct at the most fundamental level? Recall that some kind of "coarse-graining" is needed to show that entropy increases with time – for otherwise Liouville's theorem in classical statistical mechanics and unitary invariance in quantum statistical mechanics will lead to *no* entropy increase. Coarse graining is a difficult problem classically; quantum-mechanically it is even more ambiguous.

**Example 5.** As we know well, ordinary matter interacts constantly with the *electromagnetic radiation field*, in classical as well as in quantum mechanics. A primary example of the success of *quantum* statistical mechanics is Planck's law of 1900 for photon distributions in thermal equilibrium (black-body radiation), which is well verified experimentally (even on the scale of the cosmos).

Where is this interaction to be found in classical or in quantum statistical mechanics? It is not small but it is mostly ignored (except for special cases, like the laser). If there is any realistic hope of understanding the effects of this interaction, the *quantized nature* of the electromagnetic field has to be taken into account. But no one seems to know how to do this outside of perturbation theory, which is manifestly not satisfactory for  $10^{23}$  particles, and most likely not convergent.

Let me summarize what I have said so far in this way: Boltzmann's great ideas are correct, but they are often presented to students of the subject as a *fundamental theory*, which they are not. While physical systems can often be mimicked by classical models, the underlying reality is quantum-mechanical and it is less deterministic than envisaged by Boltzmann and followers. Boltzmann's view of the world has been more successful than he would have imagined, but students should be taught that there are still questions to be answered.

Before leaving the subject of quantum mechanics, let me note the irony that quantum-mechanical models pervade classical thinking more than is usually acknowledged. Many of the major successes of classical statistical mechanics, especially the mathematically rigorous, as well as computational parts of the subject, come from intrinsically quantum-mechanical models with finite, simple state spaces, of which the Ising model is the paradigm. Continuum models are notoriously difficult to analyze, and it is only relatively recently that it has been possible to prove rigorously that a phase transition occurs in a semi-realistic looking continuum model [8].

## 2 The second law of thermodynamics

The first question raised in the introduction was: What, precisely, are the thermodynamic laws that one wants to derive? I want to focus on the second law here, which, of course, is intimately related to the zeroth law (existence of thermal equilibrium). The usual approach to a "derivation" is to show that the entropy of a Hamiltonian system increases

with time – the  $H$ -theorem. My point here is that there is more to the question than this.

The second law, as understood before Boltzmann by Clausius, referred to the efficiency of steam engines and the impossibility of making heat run uphill without troubling the rest of the universe. Instead of generalizing this “law”, research somehow got narrowed into the question of showing that a macroscopic system of molecules, with deterministic dynamics governed by a Hamiltonian, would fill as much of phase space over the course of time as was consistent with whatever constraints, such as conservation of energy, were imposed on the system. A prototypical example is that a hole in a container of gas, leading to a larger container, will eventually lead to a state in which the gas is no longer confined to the small container but is uniformly spread out in the larger container.

In other words, mechanics (classical or quantum) plus some mechanism like coarse-graining drives a system to fill all available phase space (or at least fill a portion of it that is representative of the whole). This is Boltzmann’s beautiful picture, but I will discuss a realistic generalization [10] that includes this paradigm as a *special case*.

To start with, we assume that there are isolated systems in the world and that each can have various *equilibrium* states. These primitive and irreducible concepts are common to any theory. A typical state of a system is denoted by  $X$ . We consider all possible experiments which can be performed with all possible clever experimenters and all possible apparatus’s, so that at the end of the day the system is again in some *equilibrium* state  $Y$  and the *only other thing* that has possibly changed in the universe is that a weight has been lowered or raised in a gravitational field (or a spring has been compressed or stretched). Included in this is the possibility that the system may have substantially changed its nature, e.g., a chemical reaction or a mixing may have occurred.

The *key point* to note here is that the experiment need not be carried out smoothly or slowly. Violence is allowed. *Often, the system plus experimental apparatus is not even describable by a Hamiltonian in any meaningful sense!* Indeed, the intervention of an infinitely clever experimenter is permitted, one who manipulates the experiment as it develops over time. This means that a dynamical, deterministic description would have to include “free will”, or whatever it is that allows us to plan and execute experiments. I suspect this goes beyond anything contemplated by Boltzmann. It certainly goes beyond what is routinely reported in our elementary textbooks, which describe entropy and the second law in terms of quasistatic processes that never stray far from equilibrium. Nevertheless, messy, violent processes describe the real world in which the second law is supposed to be valid with *unfailing* accuracy.

It might also mean that it is difficult, if not impossible, to define the entropy of a system when it is in transit between two equilibrium states, and hence the notion of ‘increasing entropy’ might not be a fundamental concept. Only the entropy of the equilibrium states at the beginning and the end of the day are fundamental – although approximate notions of entropy in between might be useful, but inexact.

When a state change is possible from  $X$  to  $Y$  in the manner just described we write

$$X \prec Y. \quad (4)$$

Now imagine the list of all possible pairs of states  $X \prec Y$ , of all possible systems, that can be obtained in all possible experiments satisfying the stated rules. For us, the second law of thermodynamics is the ***entropy principle***, which states that this list can be *quantified* by a real-valued function on states (called “entropy”), and denoted by

$$S(X), \quad (5)$$

such that the pair  $X \prec Y$  occurs in the  $\prec$  list if and only if

$$S(X) \leq S(Y) \quad (6)$$

(but subject to the obvious constraint that the amount of each of the species in the periodic table is not changed).

What properties of the list of experimental outcomes (i.e., pairs  $X \prec Y$ ) have to be assumed in order that the list can be quantified in terms of a function in this way? It turns out that very little is needed – apart from some fairly obvious, noncontroversial assumptions. The *first law* (conservation of energy) and a weak version of the *zeroth law* (the notion of thermal equilibrium, but without mentioning temperature; see below) play an important role. It is also important (in order that  $S(X)$  is not just the constant function), that for each  $X$  there is at least one  $Y$  so that  $X \prec Y$  is on the list, but not  $Y \prec X$ .

An important consideration, however, is that the entropy function  $S(X)$  must be ***unique*** (up to a change of units) in order to be useful, but, this, too, can be verified. The importance of uniqueness comes from the need to have all definitions of entropy, including the usual ones using calorimeters and quasistatic processes, lead to the same numerical value.

The list of assumptions needed to derive the entropy principle, and the method of constructing the entropy function itself, are described in [10]. The full details are in [11]. It turns out that the construction of  $S$  is very general and does not at all need the usual coordinates, such as energy  $U$  and volume  $V$ , to parametrize the equilibrium states. An assumption, called the ‘comparison principle’ (which, in essence, states that given any two states of the same chemical composition at least one is adiabatically accessible from the other) is needed to establish the uniqueness of  $S$ . (It seems to have been first used by Landsberg [7], but reintroduced by Buchdahl, Falk and Jung, and by Giles [4].) With the introduction of the usual  $U$ ,  $V$  coordinates, however, this comparison principle can be promoted from an assumption to a theorem [10] and the uniqueness of  $S$  established.

A difficult (and insufficiently emphasized) fact is that the entropy for several mutually isolated systems is just the sum of the entropies of the individual systems. This is a consequence of the zeroth law, which is the notion of thermal equilibrium, i.e., that there is always a way to divide up a total given energy  $U$  between two systems in such a way that the resulting compound state lies above (in the sense of  $\prec$ ) all other ways of dividing the energy. Boltzmann’s formula for entropy (or von Neumann’s formula quantum-mechanically) automatically has this additivity feature.

While additivity is completely clear for the total energy (essentially because of the first law), it is not at all obvious for entropy. Suppose, for example, that we have two

systems in states  $X_1$  and  $X_2$ , respectively. Now we perform an experiment, as described above, allowing for the possibility that the two systems interact with each other during the experiment. At the end of the day the systems are again separated and found to be in states  $Y_1$  and  $Y_2$ . The entropy principle, plus the additivity of the entropy functions  $S_1$  and  $S_2$ , tell us that this event can occur if and only if

$$S_1(X_1) + S_2(X_2) \leq S_1(Y_1) + S_2(Y_2), \quad (7)$$

which is truly remarkable. It is possible that  $S_1(X_1) > S_1(Y_1)$ , which means that in order for the experiment to take place we must have  $S_2(X_2) < S_2(Y_2)$  by a minimum definite amount *determined by the change of state of system 1*. Two systems, for most purposes completely independent of each other, nevertheless recognize each other through their entropy functions and the second law – and there is nothing an experimenter can do to change this.

One is almost tempted to say that the most striking aspect of the second law is the additivity of entropy, which is a subject not often discussed in these terms in textbooks. Recall that the entropy function of a single system is defined only up to a multiplicative constant (the scaling) and up to an additive constant (the entropy at  $T = 0$ ). The additivity of entropy implies, among other things, the ability to adjust the constants of *each* system, once and for all, so that every *pair* of systems is correctly calibrated and (7) holds.

It would seem that entropy and, for all practical purposes, the second law is very general and will accompany any sufficiently rich theory, as Kadanoff implied. It need not be tied to any particular sort of dynamics, or to any notion of phase-space volume (which is problematic quantum-mechanically) especially since the experiments in question are usually not themselves describable by a dynamical system. Boltzmann's great breakthrough is paradigmatic, but may not be unique.

What, then, do we have to do to “derive” the second law?

The answer could either be “nothing”, or it could be “everything”. One crucial point is that the  $\prec$  list must be sufficiently rich, meaning that there are many pairs  $X \prec Y$  on the  $\prec$  list. This richness is needed for uniqueness because one can construct sparse, but artificial lists such that there are several entropy functions that quantify the list. In our formulation it is the comparison principle that makes the  $\prec$  list rich enough. One can be content to assume the fullness of the list as part of our world, or one can try to derive it from some more fundamental principles, which would not be easy to do.

Another, perhaps more difficult point is that the list must be *reproducible*. That is to say all permissible experiments, with all possible experimenters, always lead to exactly *one* of the following four conclusions for a given pair of states  $X$  and  $Y$ : either  $X \prec Y$  or  $Y \prec X$  or both or neither. One can either choose to assume this ‘fact’, or one can choose to prove it from some dynamics – which is an impossible task that I am not even sure how to formulate in mathematical terms. Nevertheless, *a proof of this uniqueness is almost the same as a derivation of the second law*.

In summary, the second law would appear to be a general fact about interacting systems. It is independent of any details of the dynamics, but nevertheless somehow

crucially requires non-trivial dynamics. Boltzmann's identification of entropy as the logarithm of the area of the energy surface (when suitably revised in quantum-mechanical language) was a crucial insight about many systems, but the reason that this quantity obeys the second law, and the reason for the existence of the second law, are different questions.

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Ludwig Boltzmann as a student together with friends in Vienna  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)



Ludwig Boltzmann together with fellow students  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)

# Entropy, nonequilibrium, chaos and infinitesimals

Giovanni Gallavotti

## 1 Boltzmann and entropy

Since the earliest works Boltzmann aimed at a microscopic interpretation or “proof” of the newly formulated second Law of Thermodynamics and of the associated concept of *entropy*, [1]. At the time, since the works of Bernoulli, Avogadro, Herapath, Waterstone, Krönig, Clausius it was well established that there should be an identification between absolute temperature and average kinetic energy at least in gas theory.

Boltzmann starts in [1] by stating clearly that in general (*i.e.*, not only for gases) temperature and average kinetic energy must be identified and gives a derivation of the second law for isochoric (*i.e.*, constant volume) transformations. This first derivation makes use of a periodicity assumption on the motion of (each) gas particle to obtain the existence of the time average of the kinetic energy and seems to fail if the motions are not periodic.

Nevertheless Boltzmann insisted in conceiving aperiodic motions as periodic with infinite period: see [1] where on p. 30 one finds that “*...this explanation is nothing else but the mathematical formulation of the theorem according to which the paths that do not close themselves in any finite time can be regarded as closed in an infinite time*”. He therefore pursued the implied mechanical proof of validity of Thermodynamics to the extreme consequences.

A “proof” of the second law meant to look for properties of the trajectories in phase space of a mechanical equation of motion, like time averages of suitable observables, which could have the interpretation of thermodynamic quantities like pressure  $p$ , volume  $V$ , energy  $U$ , temperature  $T$ , entropy  $S$  and be related by the thermodynamic relations, namely

$$dS = \frac{dU + p dV}{T} \quad (1.1)$$

where  $dU$ ,  $dV$ ,  $dS$  are the variations of  $U$ ,  $V$ ,  $S$  when the control parameters of the system are infinitesimally changed.

The extreme consequence was the *ergodic hypothesis* which was first mentioned by Boltzmann around 1870, see p. 237 in [2], for the internal motion of atoms in single molecules of a gas (“*it is clear that the various gas molecules will go through all possible states of motion*” which, however, could possibly be understood from the context to be different from the ergodic hypothesis, see [3], because the molecules undergo from time to time collisions). See also p. 96 in [4] and p. xxxvii in the recent collection by Flamm [5].

Considering a collection of copies of the system alike to a large molecule, p. 284 in [6], the same assumption became what is often referred as the ergodicity property of the entire gas. It implied that, by considering all motions periodic, kinetic energy

equipartition would follow and, better (see p. 287 in [6]), even what we call now the microcanonical distribution would follow (as well as the canonical distribution). The hypothesis was taken up also by Maxwell (1879), see p. 506 in [3]).<sup>1</sup>

In this way Boltzmann was able to derive various thermodynamic consequences and a proof of equation (1.1), see [8], and was led to exhibiting a remarkable example of what later would be called a “*thermodynamic analogy*” (Section III of [8]). This meant the existence of quantities associated with the phase space of a mechanical equation of motion (typically defined as time averages over the solutions of the equations of motion), which could be given thermodynamic names like equilibrium state, pressure  $p$ , volume  $V$ , energy  $U$ , temperature  $T$ , entropy  $S$  and be related by the thermodynamic relations that are expected to hold between the physical quantities bearing the same name, namely equation (1.1).

The notion of mechanical thermodynamic analogy was formulated and introduced by Helmholtz for general systems admitting only periodic motions (called *monocyclic*), [9], [10]. The proposal provided a new perspective and generated the new guiding idea that the thermodynamic relations would hold in *every mechanical system*, from the small and simple to the large and complex: in the first cases the relations would be trivial identities of no or little interest, just *thermodynamic analogies*, but in the large systems they would become nontrivial and interesting being relations of general validity. In other words they would be a kind of symmetry property of Hamiltonian mechanics.

The case of spatially confined systems with one degree of freedom was easy (easier than the example already given in [8]): with all motions periodic, the microscopic state was identified with the phase space point  $(p, q)$  representing the full mechanical state of the system, the *macroscopic state* in the corresponding thermodynamic analogy was identified with the energy surface  $H(p, q) = \frac{1}{2m}p^2 + \varphi_V(q) = U$ , where  $m$  is the mass and  $\varphi_V$  is the potential energy which confines the motion in position space, i.e., in  $q$ , and depends on a parameter  $V$ . The state is completely determined by two parameters  $U, V$ .

Average kinetic energy  $T = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau K(p(t))dt$  is identified with temperature; energy is identified with  $U$ : then if pressure  $p$  is defined as the time average  $\lim_{\tau \rightarrow \infty} -\frac{1}{\tau} \int_0^\tau \partial_V \varphi_V(q(t))dt$  the quantities  $T, p$  become functions  $p = p(U, V)$ ,  $T = T(U, V)$  of the parameters  $U, V$  determining the state of the system and the equation (1.1) should hold.

Indeed the limits as  $\tau \rightarrow \infty$  exist in such a simple case, in which all motions

<sup>1</sup>The paper [6] is a key work, albeit admittedly obscure: in modern notations it considers a system of equations of motion with dimension  $n$  and 0 divergence admitting  $n-k$  constants of motion,  $\varphi_{k+1}, \dots, \varphi_n$ , and are described by coordinates  $s_1, \dots, s_n$ . Then the distribution proportional to  $\prod_{j=k+1}^n \delta(\varphi_j - a_j)$ .

$\prod_{i=1}^n ds_i$  is invariant and can be written  $\prod_{i=1}^k ds_i \cdot \frac{1}{|\det \partial(\varphi_{n-k+1}, \dots, \varphi_n)|}$  where the last denominator denotes the Jacobian determinant (“last multiplier”) of  $\varphi_{n-k+1}, \dots, \varphi_k$  with respect to  $s_{k+1}, \dots, s_n$  evaluated at the given values  $a_{k+1}, \dots, a_n$  of the constants of motion (Boltzmann calls this an instance of the “last multiplier principle” of Jacobi). If the system has only one constant of motion, namely the energy  $H = \chi + \psi$  with  $\chi$  = potential energy and  $\psi$  = kinetic energy, this is the microcanonical distribution, as also recognized by Gibbs in the introduction of his book, [7] (where he quotes [6], but giving to it the title of its first section).

are periodic and confined between  $q_{\pm} = q_{\pm}(U, V)$  (where  $U = \varphi_V(q_{\pm})$ ); it is  $dt \equiv \frac{dq}{|\dot{q}|} = \frac{dq}{\sqrt{2(U - \varphi_V(q))/m}}$  and the period of the oscillations is  $\tau_0 = \tau_0(U, V) = 2 \int_{q_-}^{q_+} \frac{dq}{\sqrt{2(U - \varphi_V(q))/m}}$ , hence (p. 127 in [11] and Chapter I in [12])

$$\begin{aligned} T &= \frac{2}{\tau_0} \int_{q_-(U,V)}^{q_+(U,V)} \frac{m}{2} \sqrt{\frac{2}{m}(U - \varphi_V(q))} dq, \\ p &= \frac{2}{\tau_0} \int_{q_-(U,V)}^{q_+(U,V)} \frac{\partial_V \varphi_V(q)}{\sqrt{\frac{m}{2}(U - \varphi_V(q))}} dq, \end{aligned} \quad (1.2)$$

and it is immediate to check, as in [8], that equation (1.1) is fulfilled by setting

$$S(U, V) = 2 \log \int_{H=U} pdq = 2 \log \int_{q_-(U,V)}^{q_+(U,V)} \sqrt{2m(U - \varphi_V(q))} dq. \quad (1.3)$$

The case of the central motion studied in [8] was another instance of *monocyclic* systems, *i.e.*, systems with only periodic motions.

Then in the fundamental paper [11], following and inspired by the quoted works of Helmholtz, Boltzmann was able to achieve what I would call the completion of his program of deducing the second law (1.1) from mechanics. If

- (1) the *absolute temperature*  $T$  is identified with the average kinetic energy over the periodic motion following the initial datum  $(p, q)$  of a macroscopic collection of  $N$  identical particles interacting with a quite *arbitrary* pair interaction,
- (2) the *energy*  $U$  is  $H(p, q)$  sum of kinetic and of a potential energy,
- (3) the *volume*  $V$  is the volume of the region where the positions  $q$  are confined (typically by a hard wall potential),
- (4) the *pressure*  $p$  is the average force exercised on the walls by the colliding particles,

then, from the assumption that each point would evolve periodically visiting every other point on the energy surface (*i.e.*, assuming that the system could be regarded as monocyclic, see [12] Appendix 9.3 for details) it would follow that the quantity  $p$  could be identified with the  $\langle -\partial_V \varphi_V \rangle$ , time average of  $-\partial_V \varphi_V$ , and equation (1.1) would follow as a *heat theorem*. The heat theorem would therefore be a consequence of the general properties of monocyclic systems.

This led Boltzmann to realize, in the same paper, that there were a large number of mechanical models of thermodynamics: the macroscopic states could be identified with regions of phase spaces invariant under time evolution and their points would contribute to the average values of the quantities with thermodynamic interpretation (*i.e.*,  $p, V, U, T$ ) with a weight (hence a probability) also invariant under time evolution.

Hence imagining the weights as a density function one would see the evolution as a motion of phase space points leaving the density fixed. Such distributions on phase space were called *monodic* (because they keep their identity with time or, as

we say, are invariant): and in [11] several collections of weights or *monodes* were introduced: today we call them collections of invariant distributions on phase space or *ensembles*. Among the ensembles  $\mathcal{E}$ , *i.e.*, collections of monodes, Boltzmann singled out the ensembles called *orthodes* (“behaving correctly”): they were the families of probability distributions depending on a few parameters (normally 2 for simple one component systems) such that the corresponding averages  $p, V, U, T$ , defined in (1)–(4) above, would vary when the parameters were varied causing variations  $dU, dV$  of average energy and volume in such a way that the right-hand side of equation (1.1) would be an exact differential, thereby defining the *entropy*  $S$  as a function of state, see [13], [12].

The ergodic hypothesis yields the “orthodicity” of the ensemble  $\mathcal{E}$  that today we call *microcanonical* (in [11] it was named *ergode*): but ergodicity, *i.e.*, the dynamical property that evolution would make every phase space point visit every other, was not necessary to the orthodicity proof of the ergode. In fact in [11] the relation (1.1) is proved directly without recourse to dynamical properties (as we do today, see [14], [15], [12]); and in the same way the orthodicity of the *canonical ensemble* (called *holode* in [11]) was obtained and shown to generate a thermodynamics which is equivalent to the one associated with the microcanonical ensemble.<sup>2</sup>

In the end in [6] and, in final form, in [11] the theory of ensembles and of their equivalence was born without need of the ergodic property: the still important role of the ergodic hypothesis was to guarantee that the quantities  $p, V, U, T, S$  defined by orthodic averages with respect to invariant distributions on phase space had the physical meaning implied by their names (this was true for the microcanonical ensemble by the ergodic hypothesis, and for the other ensembles by the equivalence).

At the same time entropy had received a full microscopic interpretation consistent with, but independent of, the one arising in the rarefied gases case from the *Boltzmann equation* (which can be seen as a quite independent development of Boltzmann’s work). Furthermore it became clear that the entropy could be identified, up to a universal proportionality constant  $k_B$ , with the volume of phase space enclosed by the energy surface.

Unfortunately the paper [11] has been overlooked until quite recently by many, actually by most, physicists possibly because it starts, in discussing the thermodynamic analogy, by giving the Saturn rings as an “example”: a brilliant one, certainly but perhaps discouraging for the suspicious readers of this deep and original paper on thermodynamics. See p. 242 and p. 368 in [16] for an exception, perhaps the first.

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<sup>2</sup>Still today a different interpretation of the word “ensemble” is widely used: the above is based on what Boltzmann calls “*Gattung von Monoden*”, see p. 132, l. 14, of [11]: unfortunately he is not really consistent in the use of the name “monode” because, for instance in p. 134 of the same reference, he clearly calls “monode” a collection of invariant distributions rather than a single one; further confusion is generated by a typo on p. 132, l. 22, where the word “ergode” is used instead of “holode” while the “ergode” is defined only on p. 134. It seems beyond doubt that “holode” and “ergode” were intended by Boltzmann to be *collections*  $\mathcal{E}$  of invariant distributions (parameterized respectively by  $U, V$  or by  $(k_B T)^{-1}, V$  in modern notations); Gibbs instead called “ensemble” each single invariant distribution, or at least that is what is often stated. It seems that the original names proposed by Boltzmann are more appropriate, but of course we must accept calling “microcanonical ensemble” the ergode and “canonical ensemble” the holode, see [12].

## 2 Boltzmann's discrete vision of the ergodic problem

The ergodic hypothesis could not possibly say that every point of the energy surface in phase space visits in due time (the *recurrence time*) every other, see also p. 505 and following in [3]. But this statement was attributed to Boltzmann and criticized over and over again (even by Physicists, including in the influential book, [17], although enlightened mathematicians could see better, see p. 385 in [16]): however for Boltzmann phase space was discrete and points in phase space were *cells*  $\Delta$  with finite size, that I will call  $h$ . And time evolution was a permutation of the cells: ergodicity meant therefore that the permutation was a *one cycle permutation*.

This conception, perfectly meaningful mathematically, was apparently completely misunderstood by his critics: yet it was clearly stated in one of the replies to Zermelo, [18], and in the book on gases, [19], see also [13] and the de Courtenay's communication in this Symposium.

In order to explain how a reversible dynamics could be compatible with the irreversibility of macroscopic phenomena he had, in fact, to estimate the recurrence time. This was done by multiplying the typical time over which a microscopic event (*i.e.*, a collision) generates a variation of the coordinates of an order of magnitude appreciable on microscopic scales (*i.e.*, a time interval of  $\sim 10^{-12}$ s and a coordinate variation of the order of 1Å) times the number of cells into which phase space was imagined to be subdivided.

The latter number was obtained by dividing the phase space around the energy surface into equal boxes of a size  $h$  equal to the  $3N$ -th power of  $\rho^{-\frac{1}{3}}$  times  $\sqrt{mk_B T}$  with  $\rho$  the numerical density and  $k_B$  Boltzmann's constant and  $T$  temperature. With the data for  $H_2$  at normal conditions in 1cm<sup>3</sup> an earlier estimate of Thomson, [20], was rederived (and a recurrence time scale so large that it would be immaterial to measure it in seconds or in ages of the Universe).

Of course conceiving phase space as discrete is essential to formulate the ergodicity property in an acceptable way: it does not, however, make it easier to prove it even in the discrete sense just mentioned (nor in the sense acquired later when it was formulated mathematically for systems with continuous phase space). It is in fact very difficult to be *a priori* sure that the dynamics is an evolution which has only one cycle. Actually this is very doubtful: as one realizes if one attempts a numerical simulation of an equation of motion which generates motions which are ergodic in the mathematical sense.

And the difficulty is already manifest in the simpler problem of simulating differential equations in a way which rigorously respects the uniqueness theorem. In computers the microscopic states are rigorously realized as cells (because points are described by integers, so that the cells sizes are limited by the precision of hardware and software) and phase space is finite. By construction simulation programs map a cell into another: but it is extremely difficult, and possible only in very special cases (among which the only nontrivial that I know is [21]) without dedicating an inordinate computing time to insure a 1-1 correspondence between the cells.

Nevertheless the idea that phase space is discrete and motion is a permutation of its points is very appealing because it gives a privileged role to the *uniform distribution*

on the phase space region in which the motion develops (*i.e.*, the energy surface, if the ergodic hypothesis holds). However it is necessary, for consistency, that the phase space cells volume does not change with time, see Chapter 1 in [12]: this is a property that holds for Hamiltonian evolutions and therefore allows us to imagine the ergodic hypothesis as consistent with the predictions of statistical mechanics.

### 3 Boltzmann's heritage

The success of the ergodic hypothesis has several aspects. One that will not be considered further is that it is not necessary: this is quite clear as in the end we want to find the relations between a very limited number of observables and we do not need for that an assumption which tells us the values of all possible averages, most of which concern “wild” observables (like the position of a tagged particle). The consequence is that the ergodic hypothesis is intended in the sense that confined Hamiltonian systems “can be regarded as ergodic for the purpose of studying their equilibrium properties”.

What is, perhaps, the most interesting aspect of the hypothesis is that it can hold for systems of any size and lead to relations which are essentially size independent as well as model independent and which become interesting properties when considered for macroscopic systems.

*Is it possible to follow the same path in studying nonequilibrium phenomena?* The simplest such phenomena arise in stationary states of systems subject to the action of nonconservative forces and of suitable heat removing forces (whose function is to forbid indefinite build up of energy in the system).

Such states are realized in physics with great accuracy for very long times, in most cases longer than the available observation times. For instance it is possible to keep a current circulating in a wire subject to an electromotive force for a very long time, provided a suitable cooling device is attached to the wire.

As in equilibrium, the stationary states of a system will be described by a collection of probability distributions on phase space  $\mathcal{E}$ , invariant with respect to the dynamics, which I call *ensemble*: the distributions  $\mu$  in  $\mathcal{E}$  will be parameterized by a few parameters  $U, V, E_1, E_2, \dots$  which have a physical interpretation of (say) average energy, volume, intensity of the nonconservative forces acting on the system (that will be called “external parameters”). Each distribution  $\mu$  will describe a macroscopic state in which the averages of the observables will be their integrals with respect to  $\mu$ . The equations of motion will be symbolically written as

$$\dot{x} = f(x) \tag{3.1}$$

and we shall assume that  $f$  is smooth, that it depends on the external parameters and that the phase space visited by trajectories is bounded (at fixed external parameters and initial data).

Since we imagine that the system is subject to nonconservative forces the phase space volume (or any measure with density with respect to the volume) will not be

preserved by the evolution and the divergence

$$\sigma(\mathbf{x}) = - \sum_i \partial_{x_i} f_i(\mathbf{x}) \quad (3.2)$$

will be *different* from 0.

We expect that, in interesting cases, the time average  $\sigma_+$  of  $\sigma$  will be positive:

$$\sigma_+ \stackrel{\text{def}}{=} \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sigma(S_t x) dt > 0. \quad (3.3)$$

and, with few exceptions,  $x$ -independent.

This means that there cannot be invariant distributions with density with respect to the volume. And the problem to find even a single invariant distribution is nontrivial, except possibly for the ones concentrated on periodic orbits.

The problem can be attacked, possibly, by following Boltzmann's view of dynamics as discrete ("die Zahl der lebendigen Kräfte ist eine diskrete", see p. 167 in [22]).

## 4 Extending Boltzmann's ergodic hypothesis

Consider a generic "chaotic" system described by equations like (3.1) which generate motions confined in phase space. Under very general conditions it follows that  $\sigma_+ \geq 0$ , [23], and we concentrate on the case  $\sigma_+ > 0$ . The suggestion that phase space should be regarded as discrete, and motion should simply be a one-cycle permutation of the "cells"  $\Delta$  representing the phase space points is still very appealing as it would lead to the unambiguous determination of the invariant distribution  $\mu$  describing the statistical properties of the stationary states.

In fact this is an assumption implicit in any claim of physical relevance of a simulation: as already mentioned above, a computer program defines a map on small cells in phase space. Already in the case of Hamiltonian systems (*i.e.*, in equilibrium theory) a simulation will not respect the uniqueness of solutions of the equation of motion because the map between the cells will not be invertible: it is extremely hard to write a program which avoids that two distinct cells are mapped into the same cell (see above).

When  $\sigma_+ > 0$  so that, in the average, phase space volume contracts the uniqueness problem becomes essentially unsurmountable (and not only in simulations); and there will be very many cells that eventually evolve into the same cell: thus the evolution will not be a permutation of the cells. It will, however, become *eventually* a permutation of a *subset* of the initial set of cells. This reflects the fact that the orbits of the solutions of the differential equation (3.1) will "cluster" on an *attractor* which is a set of 0 volume.

The conclusion is that the statistics of the motions will still be a well defined probability distribution on phase space *provided* the ergodic hypothesis is extended to mean that the permutation of the cells on the attractor is a one-cycle permutation: it will be, in this case, still the uniform distribution concentrated on the cells lying on the attractor.

This viewpoint unifies the conception of the statistics of equilibrium and of stationary nonequilibrium: the *statistics*  $\mu$  of the motions, *i.e.*, the probability distribution  $\mu$

such that, in the continuous version of the models,

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau F(S_t x) dt = \int F(y) \mu(dy), \quad (4.1)$$

for all smooth observables  $F$  and for all but a set of zero volume of points  $x$  on phase space, can be considered, *in equilibrium as well as in stationary nonequilibrium* states, as a probability distribution which is uniform on the attractor.

The key obstacle to the above conception of statistical mechanics for stationary states is that phase space cells cannot be supposed to evolve, under the evolution assigned by equation (3.1) when  $\sigma_+ > 0$ , keeping a constant volume. Therefore regarding evolution as a map between cells of a discretized version of phase space contains new sources of possible errors. Besides the error that is present in equilibrium theory due to the cells deformations which leads to violations of the uniqueness, [12], there is an error due to their contraction  $\sigma_+ > 0$ .

In equilibrium the first error can be reduced by reducing the cells size and the time intervals at which the observations (to be interpolated into the estimate of the integral in equation (4.1)) are taken. This is a nontrivial source of errors that can be estimated to be physically acceptable, at least for the evaluation of the averages of the few observables relevant for thermodynamics, only in certain regions of the phase diagrams, see Chapter I in [12]. But at least in such regions the discrete interpretation of the ergodic hypothesis leads us to a consistent representation of the evolution as a permutation between discrete elements of a partition of phase space into small cells.

Out of equilibrium the further source of discretization error due to the actual reduction of phase space volume implies that it is not consistent to view the motion as a permutation of cells of a discretization of phase space into small equal volume elements.

Restricting attention to systems that show strongly chaotic behavior yields a possible. For instance systems which are transitive (*i.e.*, admit a dense orbit) and hyperbolic, see [24] for a formal definition, are typically chaotic systems which are also quite well understood.

To enter into some detail it is convenient to look at the time evolution by drawing a few surfaces  $\Sigma_1, \Sigma_2, \dots, \Sigma_s$  transversal to the phase space trajectories, and such that the trajectories cross some of the surfaces over and over again (*i.e.*, each trajectory crosses the surfaces infinitely many times both in the future and in the past). Let  $\Sigma = \bigcup_j \Sigma_j$  (usually called a “Poincaré section”) and let  $S$  be the map which transforms a point  $\xi \in \Sigma$  (*i.e.*, on one of the surface elements  $\Sigma_1, \Sigma_2, \dots, \Sigma_s$ ) into the point  $S\xi$  where the orbit of  $\xi$  meets again for the first time  $\Sigma$  (*i.e.*, it is again on one of the surface elements defining  $\Sigma$ ).

The points in phase space can therefore be described by pairs  $x = (\xi, \theta)$  if  $\xi$  is the point in  $\Sigma$  last visited by the trajectory starting at  $x$  and  $\theta$  is the time elapsed since that moment.

It is possible to partition  $\Sigma$  into regions  $P_1, P_2, \dots, P_n$  with the property that the symbolic dynamics histories  $\sigma = \{\sigma_i\}_{i=-\infty}^{\infty}$  on the sets  $P_\sigma$ ,  $\sigma = 1, \dots, n$ , has a *Markov property*, in the sense that

(1) there is a suitable matrix  $M_{\sigma, \sigma'}$  with entries 0 or 1, such that if  $M_{\sigma_i, \sigma_{i+1}} \equiv 1$  for all  $i$  then there is a unique point  $x$  such that  $S^i x \in P_{\sigma_i}$ : the point  $x$  is said to be “coded” by the sequence  $\sigma$ . And

(2) calling *compatible* a sequence  $\sigma$  with  $M_{\sigma_i, \sigma_{i+1}} \equiv 1$  then for all points  $x$  there is at least one compatible sequence  $\sigma$  which codes  $x$  and for all but a set of zero volume relative to  $\Sigma$  the sequence  $\sigma$  is unique (*i.e.*, much as it is the case in the binary representation of real numbers).

The partition  $P_1, P_2, \dots, P_n$  is then called a *Markov partition*: since the set of exceptions in the correspondence  $x \longleftrightarrow \sigma$  has zero volume, the volume distribution can be represented as a probability distribution  $\mu_0$  over the space of compatible sequences. And the statistics of the evolution of data  $\xi$  chosen at random with respect to the distribution  $\mu_0$ , which is the main object of interest, will therefore be represented also by a  $S$ -invariant probability distribution on the space  $\Omega$  of the compatible sequences  $\sigma$ , [24].

The sets  $P_1, P_2, \dots, P_n$  can be used to represent conveniently the microscopic states of the system: given a precision  $h > 0$  it is possible to find  $N_h$  such that the sets

$$P_{\sigma_{-N_h}, \dots, \sigma_{N_h}} = \bigcap_{j=-N_h}^{N_h} S^{-j} P_{\sigma_j} \quad (4.2)$$

have a diameter  $< h$ . Therefore the (nonempty) sets  $\Delta = P_{\sigma_{-N_h}, \dots, \sigma_{N_h}}$  can be conveniently used as “cells” to describe the evolution, when the size  $h$  is small enough for considering acceptable to neglect the variations of the (few) interesting observables within the  $\Delta$ ’s.

The evolution  $S$  will stretch  $\Delta$  along the unstable planes and compress it along the stable ones: it will map  $\Delta = P_{\sigma_{-N_h}, \dots, \sigma_{N_h}}$  inside the union of the  $n$  sets  $\bigcup_{\sigma} P_{\sigma_{-N_h+1}, \dots, \sigma_{N_h}, \sigma}$ .

We then imagine that the cell  $\Delta$  is filled by smaller boxes, that will be called *microscopic cells* or simply *microcells*, of equal volume, which under the action of  $S$  transform into boxes contained in only one of the  $n$  sets  $\Delta_{\sigma} = P_{\sigma_{-N_h+1}, \dots, \sigma_{N_h}, \sigma}$ . The microcells, which in a simulation could be identified with the integers defining them in the computer memory, should be thought of as arranged in layers adjacent to unstable planes of  $S$  and are mapped into microcells of the corresponding layers in the  $n$  cells  $\Delta_{\sigma}$ .

Since the evolution, in the average, contracts phase space the layers will merge under the action of  $S$  so that the number of microcells will initially decrease; but eventually in each cell  $\Delta$  will survive layers of microcells whose collection will be mapped one to one into itself: the latter collection of microcells is a representation of the attractor within the precision  $h$ . This is illustrated symbolically in Figure 1.

For consistency the number of microcells that is eventually found in each cell  $\Delta$  is inversely proportional to the expansion rate  $\Lambda_e(\Delta)^{-1}$  of the surface elements on the unstable manifold in  $\Delta$ : it will be denoted  $\mathcal{N} \Lambda_e(\Delta)^{-1}$ . Thus time evolution  $S$  can be represented as a permutation of the  $\mathcal{N} \sum_{\Delta} \Lambda_e(\Delta)^{-1}$  microcells on the attractor as:

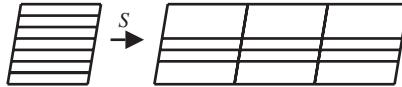


Figure 1. The lines symbolize arrays of microcells  $\Delta$ : the ones in the left drawing are horizontally stretched and merged by the time evolution into arrays that end up horizontally exactly fitting in a few new boxes, three in the picture.

- (1) give a rule to select the  $\mathcal{N}\Lambda_e(\Delta)^{-1}$  microcells in  $\Delta = P_{\sigma_{-N_h}, \dots, \sigma_{N_h}}$  and to partition them into  $n$  groups labeled by  $\sigma = 1, \dots, n$ , each containing a fraction  $\pi_\sigma = \frac{\Lambda_e^{-1}(\Delta_\sigma)}{\sum_{\sigma'} \Lambda_e^{-1}(\Delta_{\sigma'})}$  of the microcells selected in  $\Delta$ ,
- (2) establish a correspondence  $\bar{S}$  between the microcells in the group labeled  $\sigma$  and a subset the ones in  $\Delta_\sigma = P_{\sigma_{-N_h+1}, \dots, \sigma_{N_h}, \sigma}$ , and
- (3) approximate  $S$  by replacing it by  $\bar{S}$ .

Certainly there is a lot of ambiguity in deciding how to set up the selection and the correspondence: but for the purposes of a description of dynamics with precision  $h$  the ambiguity has no consequence. Note that in simulations the microcells selection is implicitly prescribed by the program, and certainly changes quite substantially by any small change of the program or by a change of the computer used. By definition of program the evolution  $S$  is replaced by a map of microcells (in huge number even in simple simulations): the map is not invertible but being a map of a finite set into itself it is eventually reduced to a permutation of a *subset* of the microcells.

Transitivity of the compatibility matrix  $M$  implies that the permutation of the microcells on the attractor can be chosen cyclic: therefore the stationary distribution  $\mu$  will be approximated by the uniform distribution on the attractor: this is a picture which seems close to Boltzmann's conception of discreteness and extends the ideas behind the ergodic hypothesis to more general dynamical systems, [25], [12].

## 5 A bit of history

The discovery of the probability distribution  $\mu$  that describes the statistics of the stationary states of dynamical systems with confined evolution did not follow the path discussed in Section 4: of course every theorem is preceded by a heuristic intuition and the exact genesis of the ideas should be asked to their authors at least to the ones present here. But there is no certainty that they will give a faithful account, as it is well known that recollection of past events in the human mind, even important ones, tends to be modified as years pass and new events occur.

We have already presented a possible history about Boltzmann's ergodic hypothesis and theory of ensembles in Sections 1 and 2.

The theory of hyperbolic transitive systems is much more recent: they were formally introduced by Anosov who proved the stability of the notion under perturbations:

a hyperbolic transitive system remains such if slightly perturbed.

The existence of a well defined statistics for almost all initial data was heralded, [26], by the work of Adler and Weiss on the area preserving map of the torus  $S(\varphi_1, \varphi_2) = (\varphi_1 + \varphi_2, \varphi_1 + 2\varphi_2)$ : they define and make use of a Markov partition. The idea was independently developed by Sinai, [27], [24], who treated the general case of an Anosov map, building Markov partitions and using them to prove the existence of a privileged distribution  $\mu$  giving the statistics of all initial data but a set of zero volume.

A remarkable property of the distribution  $\mu$  emerges when it is regarded as a probability distribution on the compatible sequences  $\sigma$  which code the points  $x$  of phase space. Namely it is a “Gibbs distribution”, in the sense of probability theory, with a short range potential: this is, essentially, a Markov process with finitely many states, *i.e.*, an object that is very well understood, [28]. The surprising consequence is that Anosov systems are “completely integrable” in the sense that we can compute essentially everything at least in principle, [29], [24]. They become a *paradigm* for chaotic evolutions in the same sense in which harmonic oscillators are a paradigm for ordered motions.

Hyperbolicity is a strong property which in practice is not satisfied in physical systems. Therefore Bowen, [30], and Ruelle, [31], [32], developed a theory for systems that are hyperbolic in a much weaker sense: these are systems with *axiom A* attractors. Also for such systems it is possible to define a natural distribution that describes the statistics of all but a set of zero volume of initial data and the distribution can be studied by an extension of Sinai’s methods.

The natural distribution has since been called the *SRB distribution* and Ruelle has proposed, in the very similar context of turbulence theory, and at least three years earlier than it appeared in print [32], [33], that in general there should be a unique distribution (or possibly a finite number of them) describing the experimental statistics of motions: it should be the distribution giving the asymptotic behavior of motions with arbitrary initial data apart from a set of zero volume.

## 6 Developments

More recently Cohen and myself, [34] and see also [12], proposed cutting a “Gordian node” by an hypothesis which extends Ruelle’s viewpoint in [35] “...while one would be very happy to prove ergodicity because it would justify the use of Gibbs’ microcanonical ensemble, real systems perhaps are not ergodic but behave nevertheless in much the same way and are well described by Gibbs’ ensemble...”:

**Chaotic Hypothesis.** *The asymptotic motions of a confined chaotic mechanical system develop on an attracting set on which motion can be considered a mixing Anosov flow.*

Of course this applies in particular to Hamiltonian systems (where the attracting set is the full energy surface) and it implies ergodicity: hence the whole body of equilibrium statistical mechanics; furthermore it puts on the same level equilibrium and non equilibrium.

This interpretation of Ruelle's ideas, [35], [33], has some applications because it implies a *formal* expression of the average values of the observables. Even though the expression is not (yet ?) computable in any interesting case it may be useful to establish relations between average values. For instance implications of a microscopic symmetry on macroscopic observables might be found from the formal (even if not practically computable) expression of the SRB distribution.

An example is obtained by considering an Anosov system  $(\mathcal{F}, S)$ , with  $\mathcal{F}$  a smooth bounded manifold and  $S$  a smooth transitive hyperbolic map of  $\mathcal{F}$ . Let

$$\sigma(x) = -\log |\det \partial_x S(x)| \quad (6.1)$$

be the phase space contraction rate and let  $\mu$  be the SRB distribution; suppose that

- (a) *dissipativity*, i.e.,  $\sigma_+ = \int \sigma(y) \mu(dy) > 0$ , and
- (b) *time reversal symmetry* in the sense that there is a smooth isometry  $I$  such that  $IS = S^{-1}I$ .

Define

$$p = \frac{1}{\tau} \sum_{j=0}^{\tau-1} \frac{\sigma(S^j x)}{\sigma_+}. \quad (6.2)$$

Then the following theorem holds, [34]:

**Fluctuation Theorem.** *With respect to the SRB distribution the observable  $p$  satisfies a large deviation property (see below) with a rate function  $\zeta(p)$  which is analytic and convex in an interval  $(-p^*, p^*)$ , for a suitable  $p^* \geq 1$ , where it exhibits the symmetry property*

$$\zeta(-p) = \zeta(p) - p\sigma_+. \quad (6.3)$$

This means that the probability  $P_{a,b}$ , in the SRB distribution  $\mu$  of  $(\mathcal{F}, S)$ , that  $p$  is in  $[a, b] \subset (-p^*, p^*)$  is such that  $\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \log P_{a,b} = \max_{p \in [a,b]} \zeta(p)$ .

Existence and analyticity of  $\zeta(p)$  is part of the quoted general results of Sinai, while the symmetry equation (6.3) was pointed out in [34] in an attempt to explain the numerical results of an earlier computer experiment [36]. The interest of the theorem lies in the fact that it is a symmetry property: hence it holds without any free parameter.

The theorem can be extended to mixing Anosov flows, [37], and therefore, via the chaotic hypothesis and if  $\sigma(x)$  is the phase space contraction rate defined in equation (3.2), it becomes a property of essentially any system which is *chaotic, dissipative and reversible*.

## 7 Entropy?

Interest in the properties of the observable  $\sigma(x)$ , equation (3.2) for flows and equation (6.2) for maps, arose in several molecular dynamics simulations in which it was naturally related to the *entropy creation rate*.

A natural question is whether a definition of entropy can be extended to nonequilibrium stationary states in analogy with the corresponding definition for equilibrium states (which are a very special case of stationary states).

The identification between the SRB distributions and distributions giving equal probability to the microcells in the attractor shows that it should be possible, at least, to define a function which is a Lyapunov function for the approach to stationarity: this would be an extension of the  $H$ -theorem of Boltzmann. However equality between the  $H$ -function evaluated in equilibrium states and thermodynamic entropy might be a coincidence, important but not extendible to non equilibrium (hence not necessary). Arguments in this direction can be found in the literature, [38], [39], and here the controversial aspects of this matter will not be touched, [40].

It will be worth however to enter into more details about why  $\sigma(x)$  has been called entropy creation rate. This is simply because in several experiments it had such an interpretation, being the ratio between a quantity that could be identified with the work per unit time done by the nonconservative forces stirring the system divided by a quantity identified with temperature of the thermostat providing the forces that extract the energy input from the stirring forces. The experiments were simulations and from many sides critiques were expressed because the interpretation seemed closely tied to the explicit form of the thermostats models, often considered “unphysical”.

Furthermore the explicit dependence on the equations of motion makes the identification of  $\sigma(x)$  with the entropy creation rate quite useless if the aim is to compare the theory with experiments different from simulations because in real experiments (*i.e.*, on experiments on matter distinct from impressive arrays of transistors) there usually is no explicit model of thermostat force and it is difficult to evaluate  $\sigma(x)$ . And it might turn out that the identification of  $\sigma(x)$  with entropy creation rate is closely related to the special models considered.

A simple, but quite general, model of thermostatted system may be useful to show that, while we should expect that there is a relation between entropy creation rate and phase space contraction, still the two notions are quite different.

The system consists in  $N \equiv N_0$  particles in a container  $\mathcal{C}_0$  and of  $N_a$  particles in  $n$  containers  $\mathcal{C}_a$  which play the role of *thermostats*: their positions will be denoted  $X_a$ ,  $a = 0, 1, \dots, n$ , and  $X \stackrel{\text{def}}{=} (X_0, X_1, \dots, X_n)$ . Interactions will be described by a potential energy

$$W(X) = \sum_{a=0}^n U_a(X_a) + \sum_{a=1}^n W_a(X_0, X_a), \quad (7.1)$$

*i.e.*, thermostats particles only interact indirectly, via the system. For simplicity, all masses will be assumed to satisfy  $m = 1$ .

The particles in  $\mathcal{C}_0$  will also be subject to external, possibly nonconservative, forces  $\mathbf{F}(X_0, \Phi)$  depending on a few strength parameters  $\Phi = (E_1, E_2, \dots)$ . It is convenient to imagine that the force due to the confining potential determining the region  $\mathcal{C}_0$  is included in  $\mathbf{F}$ , so that one of the parameters is the volume  $V = |\mathcal{C}_0|$ . See Figure 2 below.

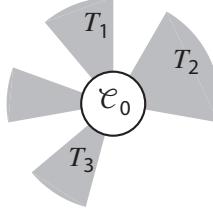


Figure 2. The reservoirs occupy finite regions outside  $\mathcal{C}_0$ , e.g., sectors  $\mathcal{C}_a \subset \mathbb{R}^3$ ,  $a = 1, 2, \dots$ . Their particles are constrained to have a *total* kinetic energy  $K_a$  constant, by suitable forces  $\vartheta_a$ , so that the reservoirs “temperatures”  $T_a$ , see equation (7.3), are well defined.

The equations of motion will be, assuming the mass  $m = 1$ ,

$$\begin{aligned}\ddot{X}_{0i} &= -\partial_i U_0(X_0) - \sum_a \partial_i U_a(X_0, X_i) + \mathbf{F}_i, \\ \ddot{X}_{ai} &= -\partial_i U_a(X_a) - \partial_i U_a(X_0, X_i) - \alpha_a \dot{X}_a,\end{aligned}\tag{7.2}$$

where the last force term  $-\alpha_a \dot{X}_a$  is a phenomenological force that implies that the thermostats particles keep constant kinetic energies:

$$K_a = \sum_{j=1}^{N_a} \frac{1}{2} (\dot{X}_j^a)^2 \stackrel{\text{def}}{=} \frac{3}{2} N_a k_B T_a \stackrel{\text{def}}{=} \frac{3}{2} N_a \beta_a^{-1},\tag{7.3}$$

where the parameters  $T_a$  should define the thermostats *temperatures* and  $\alpha_a$  can, for instance, be defined by

$$-\alpha_a \stackrel{\text{def}}{=} \frac{L_a - \dot{U}_a}{3 N_a k_B T_a}\tag{7.4}$$

where  $L_a = -\partial_{X_a} W_a(X_0, X_a) \cdot \dot{X}_a$  is the work done per unit time by the forces that the particles in  $\mathcal{C}_0$  exert on the particles in  $\mathcal{C}_a$ .

The exact form of the forces that have to be added in order to insure the kinetic energies constancy should not really matter, within wide limits. But this is a property that is not obvious and which is much debated. The above thermostating forces choice is dictated by Gauss’ *least effort* principle for the constraints  $K_a = \text{const}$ , see appendix 9.4 in [12]: this is a criterion that has been adopted in several simulations, [41]. Independently of Gauss’ principle it is immediate to check that if  $\alpha_a$  is defined by equation (7.4) then the kinetic energies  $K_a$  are strictly constants of motion.

The work  $L_a$  in equation (7.4) will be interpreted as *heat*  $\dot{Q}_a$  ceded, per unit time, by the particles in  $\mathcal{C}_0$  to the  $a$ -th thermostat (because the “temperature” of  $\mathcal{C}_a$  remains constant, hence the thermostats can be regarded in thermal equilibrium). The *entropy creation rate* due to heat exchanges between the system and the thermostats can, therefore, be naturally defined as

$$\sigma^0(\dot{X}, X) \stackrel{\text{def}}{=} \sum_{a=1}^{N_a} \frac{\dot{Q}_a}{k_B T_a}.\tag{7.5}$$

It should be stressed that here *no entropy notion* is introduced for the stationary state: only variation of the thermostats entropy is considered and it should not be regarded as a new quantity because the thermostats should be considered in equilibrium at a fixed temperature.

The question is whether there is any relation between  $\sigma_0$  and the phase space contraction  $\sigma$  of equation (3.2). The latter can be immediately computed and is (neglecting  $O(\min_{a>0} N_a^{-1})$ )

$$\sigma^\Gamma(\dot{X}, X) = \sum_{a>0} \frac{3N_a - 1}{3N_a} \frac{\dot{Q}_a - \dot{U}_a}{k_B T_a} = \sum_{a>0} \frac{\dot{Q}_a}{k_B T_a} - \dot{U} \quad (7.6)$$

where  $U = \sum_{a>0} \frac{3N_a - 1}{3N_a} \frac{U_a}{k_B T_a}$ . Hence in this example in which the thermostats are “external” to the system volume (unlike to what happens in the common examples in which they act inside the volume of the system), the phase space contraction is not the entropy creation rate, [42]. *However it differs from the entropy creation rate by a total derivative.*

The latter remark implies that if the chaotic hypothesis is accepted for the system in Figure 2 then, assuming  $U_a$  bounded (for simplicity, see [43], [42] for more general cases) it is  $\sigma_+ = \langle \sigma_0 \rangle$  because the derivative  $\dot{U}$  contributes  $\frac{1}{\tau}(U(\tau) - U(0)) \xrightarrow{\tau \rightarrow \infty} 0$  and also the observable  $p$ , in the continuous time extension of equation (6.2), [37], has the same rate function as the observable  $p = \frac{1}{\tau} \int_0^\tau \sigma_0(S_t x) dt \equiv \frac{1}{\tau} \int_0^\tau \sigma(S_t x) dt + O(\tau^{-1})$ . Since the equations of motion (7.2) are time reversible (a rather general property of Gaussian constraints, with  $I$  being here simply velocity reversal) it follows that *the “physical entropy creation” equation (7.5) has a fluctuation rate  $\zeta(p)$  satisfying the fluctuation relation equation (6.3).*

This is relevant because the definition equation (7.5) has meaning independently of the equations of motions and can therefore be suitable for experimental tests. [44], [42]. The above is just a model of thermostats: other interesting models have been proposed based on purely Hamiltonian interactions at the price of relying on thermostats of infinite size, see [45], [46], [47].

## 8 Extensions of Boltzmann’s $H$ -theorem

The above analysis *does not require a notion of entropy* to be defined for stationary states.

There is, however, another key contribution of Boltzmann to statistical mechanics, briefly mentioned above. This is the Boltzmann’s equation and the relative  *$H$ -theorem*, [48].

The theorem has attracted deep interest because of its philosophical implications. For our purposes it is important because it provides a theory of approach to equilibrium and therefore it is one of the first results on nonequilibrium.

It is useful to stress that the definition of  $H$  is given in the context of the approach to equilibrium and Boltzmann never applied it (nor, perhaps, meant to apply it) to the

approach to other stationary states and to their theory. The equality of the value of  $H$  with the thermodynamic entropy when evaluated on the equilibrium state raised the hope that it could be possible to define entropy for systems out of equilibrium and even if not in stationary state. The idea emerged clearly already from the foundational papers on the Boltzmann equation (“*log P was well defined whether or not the system is in equilibrium, so that it could serve as a suitable generalization of entropy*”, p. 82 in [49] and p. 218 in [22]) and many attempts can be found in the literature to define entropy for systems out of equilibrium in stationary states or even in macroscopically evolving states.

Strictly speaking the implication that can be drawn from the works on the Boltzmann’s equation is that a rarefied gas started in a given configuration evolves in time so that the average values of the observables, at least of the few of interest, acquire an asymptotic value which is the same as the one that can be computed from a probability distribution maximizing a function  $H$ .

The acquisition of an asymptotic value by the averages of the observables is a property expected to hold also when the asymptotic state is a nonequilibrium stationary state. And it is natural to think that also in such cases there will be a function that approaches monotonically an asymptotic value signaling that the few observables of interest approach their asymptotic average.

As remarked above the SRB distribution is a uniform distribution over the attractor: therefore it verifies a variational property and this can be used to define a Lyapunov function that evolves towards a maximum, [38]. Let  $\eta = (\sigma_{-N_h}, \dots, \sigma_{N_h})$  and  $H \stackrel{\text{def}}{=} \frac{1}{\tau} \sum_{\eta} -p_{\eta} (\log p_{\eta} + \log \Lambda_{\tau}(\eta^{-1}))$  where  $p_{\eta}$  denotes the fraction of microcells that can be found in the cell  $\Delta = P_{\eta} = \bigcap_{k=-N_h}^{N_h} S^{-k} P_{\eta_k}$  after a time of  $\tau$  units has elapsed starting from an initial distribution  $p_{\eta}^0$  (typically a uniform distribution over the microcells in a single cell  $\Delta^0$ ). This is a quantity that tends to a maximum as time evolves (reaching it when the  $p_{\eta}$  have the value of the SRB distribution and the maximum equals, therefore, the logarithm of the number of microcells on the attractor).

Therefore the quantity  $H$  tends in the average to a maximum and it can be regarded as an instance of an  $H$ -function. However the maximum depends on the precision  $h$  of the *coarse graining* defined by the partition of phase space by the cells  $\Delta$ . Changing the precision several changes occur which have to be examined if a meaning other than that of a Lyapunov function has to be given to  $H$ . The analysis in [38] points out that  $H$  changes with the precision  $h$  in a trivial way (*i.e.*, by an additive constant, independent of the control parameters of the system and depending only on the precision  $h$  which is customarily chosen equal to Planck’s constant after the rise of quantum mechanics) if the SRB state on which it is evaluated is an equilibrium state. In the latter case it is proportional to the logarithm of the phase space volume that can be visited. In the nonequilibrium cases however  $H$  changes when the precision  $h$  changes by additive quantities that *are not just functions of h* but depend on thermodynamic quantities (like average energy, temperatures, *etc.*), [38].

This indicates that while not excluding the possibility of existence of Lyapunov functions, see [50], indicating the approach to equilibrium (within a given precision  $h$ )

the identity of the  $H$ -function with entropy, *i.e.*, its identity with a function of the state parameters of the system, is possible only when the state is in an equilibrium state. My interpretation of this analysis, based once more on a discrete point of view on the problem, is that one should not insist in looking for a notion of entropy in systems out of equilibrium, [38].

If so once again Boltzmann's attitude to consider phase space as discrete and in general to deny reality to the continua might have led to insights into difficult questions.

## 9 Conclusion

Boltzmann's contribution to the theory of ensembles and to the mechanical interpretation of heat and thermodynamics was based on a discrete conception of the continuum: his staunch coherence on this view has been an essential aspect of the originality of his thought.

It is in fact a method of investigation which is still very fruitful and used in various forms when “cut-offs” or “regularizations” are employed in the most diverse fields. In my view it has been and still is important in the recent developments in the theory of nonequilibrium stationary states. The Fluctuation Theorem and its various interpretations, extensions and applications (to Onsager reciprocity at non zero forcing, to Green–Kubo formulae, to fluid mechanics, turbulence and intermittency, see [12], [51], [24]) is, hopefully, only an example.

It is interesting in this context recall a few quotes from Boltzmann:

*“Through the symbols manipulations of integral calculus, which have become common practice, one can temporarily forget the need to start from a finite number of elements, that is at the basis of the creation of the concept, but one cannot avoid it.”;*

see p. 227 in [52], and on the same page:

*“Differential equations require, just as atomism does, an initial idea of a large finite number of numerical values and points ... Only afterwards it is maintained that the picture never represents phenomena exactly but merely approximates them more and more the greater the number of these points and the smaller the distance between them. Yet here again it seems to me that so far we cannot exclude the possibility that for a certain very large number of points the picture will best represent phenomena and that for greater numbers it will become again less accurate, so that atoms do exist in large but finite number.”;*

and see p. 55 in [52]:

*“This naturally does not exclude that, after we got used once and for all to the abstraction of the volume elements and of the other symbols [of Calculus] and once one has studied the way to operate with them, it could*

*look handy and luring, in deriving certain formulae that Volkmann calls formulae for the coarse phenomena, to forget completely the atomistic significance of such abstractions. They provide a general model for all cases in which one can think to deal with  $10^{10}$  or  $10^{10^{10}}$  elements in a cubic millimeter or even with billions of times more; hence they are particularly invaluable in the frame of Geometry, which must equally well adapt to deal with the most diverse physical cases in which the number of the elements can be widely different. Often in the use of all such models, created in this way, it is necessary to put aside the basic concept, from which they have overgrown, and perhaps to forget it entirely, at least temporarily. But I think that it would be a mistake to think that one could become free of it entirely.”*

And the principle was really applied not only in the conception of the ergodic hypothesis, [2], [6], but also in the deduction of the Boltzmann's equation which Boltzmann felt would be clarified by following discretization methods (in energy) inspired by those employed in the “*elegant solution of the problem of string-vibrations*” of Lagrange, or in Stefan's study of diffusion or in Riemann's theory of mean curvature, [48] and in various discussions of the heat theorem, [22].

The above conception of the *infinitesimal quantities*, rooted in the early days of Calculus when “ $dx$ ” was regarded as *infinitely small and yet still of finite size* (in apparent, familiar, logical contradiction), is an important legacy that should not be forgotten in spite of the social pressure that induces all of us to identify clarity of physical understanding with continuous models of reality.

## Appendix: Temperature and kinetic energy, [3], [16]

The first attempts at a kinetic explanation of the properties of gases came following the experiments by Boyle (1660), on the gas compression laws. The laws established that “air” had elastic properties and that there was inverse proportionality between pressure and volume: a theory that was considered also by Newton. It was D. Bernoulli (1720), who abandoned the view, espoused by Newton, that the atoms were arranged on a kind of lattice repelling each other (with a force inversely proportional to their distances to agree with Boyle's law, but extending only to the nearest neighbors). Bernoulli imagined the atoms to be free and that pressure was due to the collisions with the walls and proportional to the square of the average speed proposing that a correct definition of temperature should be based on this property.

In 1816 Avogadro established that, for rarefied gases, the ratio  $pV/T$  is proportional to the number of atoms or molecules via a universal constant. This was a striking result, explaining the anomalies in the earlier theory of Dalton and allowing, besides the definition of the *Avogadro's number*, the correct determination of the relative molecular and atomic weights. It opened the way to the definition of absolute temperature, independently of the special gas-thermometer employed, and to the principle of energy equipartition and to the later works of Waterstone, Clausius, Boltzmann, among others.

The attempt of Laplace, (1821), proposed an elaborate scheme in which the atoms, still essentially fixed in space at average distance  $r$  would contain a quantity  $c$  of *caloric* and would interact with a short range force proportional to the product of their quantity of caloric and depending on the distance. Identifying the caloric  $c$  with the fixed amount contained in each atom would have led to a gas law with  $p$  proportional to the square of the density  $\rho$ , *i.e.*, to  $\rho^2 c^2$ ; but this was avoided by supposing that the amount of caloric  $c$  in each molecule was determined by an equilibrium between the amount of caloric emitted by a molecule and the caloric received by it (emitted from the other molecules) concluding, via an argument (criticized by many commentators) that  $\rho c^2$  should depend solely on temperature, see [3].

The theory of Laplace did not sound convincing and the work of Bernoulli went unnoticed; the same was the fate of the work of Herapath (1820), who again proposed, without knowing Bernoulli's theory, that the atoms were free and pressure was due to collisions with the walls; however he assumed that pressure was proportional to the average momentum rather than kinetic energy obtaining an incorrect definition of absolute temperature. In any event his work was rejected by the *Philosophical transactions of the Royal Society of London* and published on the *Annals of Philosophy* falling into oblivion for a while.

In 1845 Waterstone, unaware of Bernoulli and Herapath but (likely) familiar with Avogadro's work, proposed the theory of gases with the correct identification of pressure as proportional to the average kinetic energy and the density, introducing also a rather detailed conception of the interatomic forces taking up ideas inspired by Mossotti (who probably had also made Avogadro and Italian science better known in England during his political exile). Unfortunately he submitted it to the *Philosophical transactions of the Royal Society* which readily rejected it and remained unpublished, until it was rediscovered much later (1892, by Rayleigh).

In the 1840s, through the work of Meyer, Joule, Helmholtz and others the energy conservation principle was established with the consequent identification of heat as a form of energy convertible into mechanical work forcing (reasonable) physicists to abandon the hypothesis of the existence of caloric as a conserved entity.

The theory of gases begun to be really accepted with the work of Krönig (1856), who clearly proposed identifying temperature with average kinetic energy of molecules. His work became well known as it appeared to have prompted the publication of Clausius's paper of (1857), who had independently reached the same conclusions and gone much further. Not only Clausius went quite far in establishing energy equipartition (completed by Maxwell in 1860) but he introduced a basic concept of kinetic theory: the mean free path. Thus making clear the role of collisions in gas theory: they lead to prediction and to a first understanding of the phenomenon of diffusion, explaining the apparent paradoxes linked to the earlier assumptions that in rarefied gases collisions could be simply neglected, and also initiate the theory of the transport coefficients.

The latter papers, one century after the too far in advance (over his time) work of Bernoulli, gave origin to kinetic theory in the sense we intend it still now, and stimulated also the related investigations of Maxwell. Therefore Maxwell (1859) and a little later Boltzmann (1866) could start their work taking for granted the well established

identity between temperature and average kinetic energy for gases extending it to hold in all systems in equilibrium (rarefied or not). This key view was not destined to have a long life: the advent of quantum mechanics would prove that proportionality between average kinetic energy and temperature could only be approximate and to hold if quantum corrections to atomic mechanics were negligible, see [12]. Nevertheless the identification of temperature and kinetic energy plaid (and still plays, whenever quantum effects are negligible) an essential role not only in classical statistical mechanics but also in the discovery of quantum mechanics, which was heralded by the failure of the related equipartition of energy.

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Josef Loschmidt (1821–1895)  
(Courtesy of the Österreichische Zentralbibliothek für Physik)



Ludwig Boltzmann in Vienna 1875  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)

# **From time-symmetric microscopic dynamics to time-asymmetric macroscopic behavior: an overview**

Joel L. Lebowitz

## **Introduction**

Let me start by stating clearly that I am not going to discuss here – much less claim to resolve – the many complex issues, philosophical and physical, concerning the nature of time, from the way we perceive it to the way it enters into the space-time structure in relativistic theories. I will also not try to philosophize about the “true” nature of probability. My goal here, as in my previous articles [1], [2] on this subject, is much more modest.<sup>1</sup> I will take (our everyday notions of) space, time and probability as primitive undefined concepts and try to clarify the many conceptual and mathematical problems encountered in going from a time symmetric Hamiltonian microscopic dynamics to a time asymmetric macroscopic one, as given for example by the diffusion equation. I will also take it for granted that every bit of macroscopic matter is composed of an enormous number of quasi-autonomous units, called atoms (or molecules).

The atoms, taken to be the basic entities making up these macroscopic objects, will be simplified to the point of caricature: they will be treated, to quote Feynman [3], as “little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.” This crude picture of atoms (a refined version of that held by some ancient Greek philosophers) moving according to non-relativistic classical Hamiltonian equations contains the essential qualitative and even quantitative ingredients of macroscopic irreversibility. To accord with our understanding of microscopic reality it must, of course, be modified to take account of quantum mechanics. This raises further issues for the question of irreversibility which will be discussed in Section 9.

Much of what I have to say is a summary and elaboration of the work done over a century ago, when the problem of reconciling time asymmetric macroscopic behavior with the time symmetric microscopic dynamics became a central issue in physics. To quote from Thomson’s (later Lord Kelvin) beautiful and highly recommended 1874 article [4], [5] “The essence of Joule’s discovery is the subjection of physical [read thermal] phenomena to [microscopic] dynamical law. If, then, the motion of every particle of matter in the universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after. The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water .... Physical processes, on the other hand, are irreversible: for example, the friction of solids, conduction of heat, and

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<sup>1</sup>The interested reader may wish to look at the three book reviews which are contained in [1e], [1f]. These books attempt to deal with some fundamental questions about time. As for the primitive notion of probability I have in mind something like this: the probability that when you next check your mail box you will find a package with a million dollars in it is very small, cf. Section 3.

diffusion. Nevertheless, the principle of dissipation of energy [irreversible behavior] is compatible with a molecular theory in which each particle is subject to the laws of abstract dynamics.”

**Formulation of the problem.** Formally the problem considered by Thomson in the context of Newtonian theory, the “theory of everything” at that time, is as follows: The complete microscopic (or micro) state of a classical system of  $N$  particles is represented by a point  $X$  in its phase space  $\Gamma$ ,  $X = (\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \dots, \mathbf{r}_N, \mathbf{p}_N)$ ,  $\mathbf{r}_i$  and  $\mathbf{p}_i$  being the position and momentum (or velocity) of the  $i$ th particle. When the system is isolated its evolution is governed by Hamiltonian dynamics with some specified Hamiltonian  $H(X)$  which we will assume for simplicity to be an even function of the momenta. Given  $H(X)$ , the microstate  $X(t_0)$ , at time  $t_0$ , determines the microstate  $X(t)$  at all future and past times  $t$  during which the system will be or was isolated:  $X(t) = T_{t-t_0}X(t_0)$ . Let  $X(t_0)$  and  $X(t_0 + \tau)$ , with  $\tau$  positive, be two such microstates. Reversing (physically or mathematically) all velocities at time  $t_0 + \tau$ , we obtain a new microstate. If we now follow the evolution for another interval  $\tau$  we find that the new microstate at time  $t_0 + 2\tau$  is just  $RX(t_0)$ , the microstate  $X(t_0)$  with all velocities reversed:  $RX = (\mathbf{r}_1, -\mathbf{p}_1, \mathbf{r}_2, -\mathbf{p}_2, \dots, \mathbf{r}_N, -\mathbf{p}_N)$ . Hence if there is an evolution, i.e. a trajectory  $X(t)$ , in which some property of the system, specified by a function  $f(X(t))$ , behaves in a certain way as  $t$  increases, then if  $f(X) = f(RX)$  there is also a trajectory in which the property evolves in the time reversed direction. Thus, for example, if particle densities get more uniform as time increases, in a way described by the diffusion equation, then since the density profile is the same for  $X$  and  $RX$  there is also an evolution in which the density gets more nonuniform. So why is one type of evolution, the one consistent with an entropy increase in accord with the “second law”, common and the other never seen? The difficulty is illustrated by the impossibility of time ordering of the snapshots in Figure 1 using *solely* the microscopic dynamical laws: the above time symmetry implies that if  $(a, b, c, d)$  is a possible ordering so is  $(d, c, b, a)$ .

**Resolution of the problem.** The explanation of this apparent paradox, due to Thomson, Maxwell and Boltzmann, as described in references [1]–[17], which I will summarize in this article, shows that *not only is there no conflict* between reversible microscopic laws and irreversible macroscopic behavior, but, as clearly pointed out by Boltzmann in his later writings<sup>2</sup>, *there are extremely strong reasons to expect the latter from the former*. These reasons involve several interrelated ingredients which together provide the required distinction between microscopic and macroscopic variables and explain the emergence of definite time asymmetric behavior in the evolution of the latter despite the total absence of such asymmetry in the dynamics of the former. They are: a) the great disparity between microscopic and macroscopic scales, b) the fact that the events

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<sup>2</sup>Boltzmann’s early writings on the subject are sometimes unclear, wrong, and even contradictory. His later writings, however, are generally very clear and right on the money (even if a bit verbose for Maxwell’s taste, cf. [8]). The presentation here is not intended to be historical.

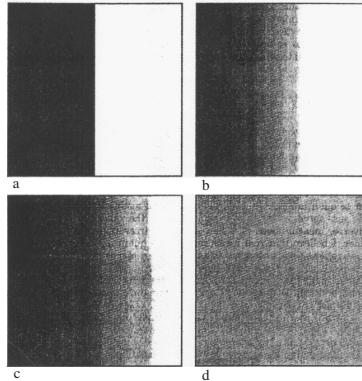


Figure 1. A sequence of “snapshots”, a, b, c, d taken at times  $t_a, t_b, t_c, t_d$ , each representing a macroscopic state of a system, say a fluid with two “differently colored” atoms or a solid in which the shading indicates the local temperature. How would you order this sequence in time?

we observe in our world are determined not only by the microscopic dynamics, but also by the initial conditions of our system, which, as we shall see later, in Section 6, are very much related to the initial conditions of our universe, and c) the fact that it is not every microscopic state of a macroscopic system that will evolve in accordance with the entropy increase predicted by the second law, but only the “majority” of such states – a majority which however becomes so overwhelming when the number of atoms in the system becomes very large that irreversible behavior becomes effectively a certainty. To make the last statement complete we shall have to specify the assignment of weights, or probabilities, to different microstates consistent with a given macrostate. Note, however, that since we are concerned with events which have overwhelming probability, many different assignments are equivalent and there is no need to worry about them unduly. There is however, as we shall see later, a “natural” choice based on phase space volume (or dimension of Hilbert space in quantum mechanics). These considerations enabled Boltzmann to define the entropy of a macroscopic system in terms of its microstate and to relate its change, as expressed by the second law, to the evolution of the system’s microstate. We detail below how the above explanation works by describing first how to specify the macrostates of a macroscopic system. It is in the time evolution of these macrostates that we observe irreversible behavior [1]–[17].

**Macrostates.** To describe the macroscopic state of a system of  $N$  atoms in a box  $V$ , say  $N \gtrsim 10^{20}$ , with the volume of  $V$ , denoted by  $|V|$ , satisfying  $|V| \gtrsim Nl^3$ , where  $l$  is a typical atomic length scale, we make use of a much cruder description than that provided by the microstate  $X$ , a point in the  $6N$  dimensional phase space  $\Gamma = V^N \otimes \mathbb{R}^{3N}$ . We shall denote by  $M$  such a macroscopic description or macrostate. As an example we may take  $M$  to consist of the specification, to within a given accuracy, of the energy and number of particles in each half of the box  $V$ . A more refined macroscopic description would divide  $V$  into  $K$  cells, where  $K$  is large but still  $K \ll N$ , and specify the

number of particles, the momentum, and the amount of energy in each cell, again with some tolerance. For many purposes it is convenient to consider cells which are small on the macroscopic scale yet contain many atoms. This leads to a description of the macrostate in terms of smooth particle, momentum and energy densities, such as those used in the Navier–Stokes equations [18], [19]. An even more refined description is obtained by considering a smoothed out density  $f(\mathbf{r}, \mathbf{p})$  in the six-dimensional position and momentum space such as enters the Boltzmann equation for dilute gases [17]. (For dense systems this needs to be supplemented by the positional potential energy density; see footnote 4 and reference [2] for details.)

Clearly  $M$  is determined by  $X$  (we will thus write  $M(X)$ ) but there are many  $X$ 's (in fact a continuum) which correspond to the same  $M$ . Let  $\Gamma_M$  be the region in  $\Gamma$  consisting of all microstates  $X$  corresponding to a given macrostate  $M$  and denote by  $|\Gamma_M| = (N!h^{3N})^{-1} \int_{\Gamma_M} \Pi_{i=1}^N d\mathbf{r}_i d\mathbf{p}_i$ , its symmetrized  $6N$  dimensional Liouville volume (in units of  $h^{3N}$ ).

**Time evolution of macrostates: an example.** Consider a situation in which a gas of  $N$  atoms with energy  $E$  (with some tolerance) is initially confined by a partition to the left half of the box  $V$ , and suppose that this constraint is removed at time  $t_a$ , see Figure 1. The phase space volume available to the system for times  $t > t_a$  is then fantastically enlarged<sup>3</sup> compared to what it was initially, roughly by a factor of  $2^N$ .

Let us now consider the macrostate of this gas as given by  $M = (\frac{N_L}{N}, \frac{E_L}{E})$ , the fraction of particles and energy in the left half of  $V$  (within some small tolerance). The macrostate at time  $t_a$ ,  $M = (1, 1)$ , will be denoted by  $M_a$ . The phase-space region  $|\Gamma| = \Sigma_E$ , available to the system for  $t > t_a$ , that is, the region in which  $H(X) \in (E, E + \delta E), \delta E \ll E$ , will contain new macrostates, corresponding to various fractions of particles and energy in the left half of the box, with phase space volumes very large compared to the initial phase space volume available to the system. We can then expect (in the absence of any obstruction, such as a hidden conservation law) that as the phase point  $X$  evolves under the unconstrained dynamics and explores the newly available regions of phase space, it will with very high probability enter a succession of new macrostates  $M$  for which  $|\Gamma_M|$  is increasing. The set of all the phase points  $X_t$ , which at time  $t_a$  were in  $\Gamma_{M_a}$ , forms a region  $T_t \Gamma_{M_a}$  whose volume is, by Liouville's Theorem, equal to  $|\Gamma_{M_a}|$ . The shape of  $T_t \Gamma_{M_a}$  will however change with  $t$  and as  $t$  increases  $T_t \Gamma_{M_a}$  will increasingly be contained in regions  $\Gamma_M$  corresponding to macrostates with larger and larger phase space volumes  $|\Gamma_M|$ . This will continue until almost all the phase points initially in  $\Gamma_{M_a}$  are contained in  $\Gamma_{M_{eq}}$ , with  $M_{eq}$  the system's unconstrained macroscopic equilibrium state. This is the state in which approximately half the particles and half the energy will be located in the left half of the box,  $M_{eq} = (\frac{1}{2}, \frac{1}{2})$  i.e.  $N_L/N$  and  $E_L/E$  will each be in an interval  $(\frac{1}{2} - \epsilon, \frac{1}{2} + \epsilon)$ ,  $N^{-1/2} \ll \epsilon \ll 1$ .

$M_{eq}$  is characterized, in fact defined, by the fact that it is the unique macrostate,

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<sup>3</sup>If the system contains 1 mole of gas then the volume ratio of the unconstrained phase space region to the constrained one is far larger than the ratio of the volume of the known universe to the volume of one proton.

among all the  $M_\alpha$ , for which  $|\Gamma_{M_{\text{eq}}}|/|\Sigma_E| \simeq 1$ , where  $|\Sigma_E|$  is the total phase space volume available under the energy constraint  $H(X) \in (E, E + \delta E)$ . (Here the symbol  $\simeq$  means equality when  $N \rightarrow \infty$ .) That there exists a macrostate containing almost all of the microstates in  $\Sigma_E$  is a consequence of the law of large numbers [20], [18]. The fact that  $N$  is enormously large for macroscopic systems is absolutely critical for the existence of thermodynamic equilibrium states for any reasonable definition of macrostates, e.g. for any  $\epsilon$ , in the above example such that  $N^{-1/2} \ll \epsilon \ll 1$ . Indeed thermodynamics does not apply (is even meaningless) for isolated systems containing just a few particles, cf. Onsager [21] and Maxwell quote in the next section [22]. Nanosystems are interesting and important intermediate cases which I shall however not discuss here; see related discussion about computer simulations in footnote 5.

After reaching  $M_{\text{eq}}$  we will (mostly) see only small fluctuations in  $N_L(t)/N$  and  $E_L(t)/E$ , about the value  $\frac{1}{2}$ : typical fluctuations in  $N_L$  and  $E_L$  being of the order of the square root of the number of particles involved [18]. (Of course if the system remains isolated long enough we will occasionally also see a return to the initial macrostate – the expected time for such a Poincaré recurrence is however much longer than the age of the universe and so is of no practical relevance when discussing the approach to equilibrium of a macroscopic system [6], [8].)

As already noted earlier the scenario in which  $|\Gamma_{M(X(t))}|$  increase with time for the  $M_a$  shown in Figure 1 cannot be true for all microstates  $X \subset \Gamma_{M_a}$ . There will of necessity be  $X$ 's in  $\Gamma_{M_a}$  which will evolve for a certain amount of time into microstates  $X(t) \equiv X_t$  such that  $|\Gamma_{M(X_t)}| < |\Gamma_{M_a}|$ , e.g. microstates  $X \in \Gamma_{M_a}$  which have all velocities directed away from the barrier which was lifted at  $t_a$ . What is true however is that the subset  $B$  of such “bad” initial states has a phase space volume which is very very small compared to that of  $\Gamma_{M_a}$ . This is what I mean when I say that entropy increasing behavior is *typical*; a more extensive discussion of typicality is given later.

## 1 Boltzmann's entropy

The end result of the time evolution in the above example, that of the fraction of particles and energy becoming and remaining essentially equal in the two halves of the container when  $N$  is large enough (and ‘exactly equal’ when  $N \rightarrow \infty$ ), is of course what is predicted by the second law of thermodynamics. According to this law the final state of an isolated system with specified constraints on the energy, volume, and mole number is one in which the entropy, a measurable macroscopic quantity of equilibrium systems, defined on a purely operational level by Clausius, has its maximum. (In practice one also fixes additional constraints, e.g. the chemical combination of nitrogen and oxygen to form complex molecules is ruled out when considering, for example, the dew point of air in the ‘equilibrium’ state of air at normal temperature and pressure, cf. [21]. There are, of course, also very long lived metastable states, e.g. glasses, which one can, for many purposes, treat as equilibrium states even though their entropy is not maximal. I will ignore these complications here.) In our example this thermodynamic entropy would be given by  $S = V_L s(\frac{N_L}{V_L}, \frac{E_L}{V_L}) + V_R s(\frac{N_R}{V_R}, \frac{E_R}{V_R})$  defined for all equilibrium

states in separate boxes  $V_L$  and  $V_R$  with given values of  $N_L$ ,  $N_R$ ,  $E_L$ ,  $E_R$ . When  $V_L$  and  $V_R$  are united to form  $V$ ,  $S$  is maximized subject to the constraint of  $E_L + E_R = E$  and of  $N_L + N_R = N$ :  $S_{\text{eq}}(N, V) = V_s(\frac{N}{V}, \frac{E}{V})$ .

It was Boltzmann's great insight to connect the second law with the above phase space volume considerations by making the observation that for a dilute gas  $\log |\Gamma_{M_{\text{eq}}}|$  is proportional, up to terms negligible in the size of the system, to the thermodynamic entropy of Clausius. Boltzmann then extended his insight about the relation between thermodynamic entropy and  $\log |\Gamma_{M_{\text{eq}}}|$  to all macroscopic systems; be they gas, liquid or solid. This provided for the first time a microscopic definition of the operationally measurable entropy of macroscopic systems in *equilibrium*.

Having made this connection Boltzmann then generalized it to define an entropy also for macroscopic systems not in equilibrium. That is, he associated with each microscopic state  $X$  of a macroscopic system a number  $S_B$  which depends only on  $M(X)$  given, up to multiplicative and additive constants (which can depend on  $N$ ), by

$$S_B(X) = S_B(M(X)) \quad (1a)$$

with

$$S_B(M) = k \log |\Gamma_M|, \quad (1b)$$

which, following O. Penrose [13], I shall call the Boltzmann entropy of a classical system:  $|\Gamma_M|$  is defined in Section 1.3. N. B. I have deliberately written (1) as two equations to emphasize their logical independence which will be useful for the discussion of quantum systems in Section 9.

Boltzmann then used phase space arguments, like those given above, to explain (in agreement with the ideas of Maxwell and Thomson) the observation, embodied in the second law of thermodynamics, that when a constraint is lifted, an isolated macroscopic system will evolve toward a state with greater entropy.<sup>4</sup> In effect Boltzmann argued that due to the large differences in the sizes of  $\Gamma_M$ ,  $S_B(X_t) = k \log |\Gamma_{M(X_t)}|$  will *typically* increase in a way which *explains* and describes qualitatively the evolution towards equilibrium of macroscopic systems.

These very large differences in the values of  $|\Gamma_M|$  for different  $M$  come from the very large number of particles (or degrees of freedom) which contribute, in an (approximately) additive way, to the specification of macrostates. This is also what gives rise to typical or almost sure behavior. Typical, as used here, means that the set of microstates corresponding to a given macrostate  $M$  for which the evolution leads to a macroscopic increase (or non-decrease) in the Boltzmann entropy during some

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<sup>4</sup>When  $M$  specifies a state of local equilibrium,  $S_B(X)$  agrees up to negligible terms, with the "hydrodynamic entropy". For systems far from equilibrium the appropriate definition of  $M$  and thus of  $S_B$  can be more problematical. For a dilute gas (with specified kinetic energy and negligible potential energy) in which  $M$  is specified by the smoothed empirical density  $f(\mathbf{r}, \mathbf{v})$  of atoms in the six dimensional position and velocity space,  $S_B(X) = -k \int f(\mathbf{r}, \mathbf{v}) \log f(\mathbf{r}, \mathbf{v}) d\mathbf{r} d\mathbf{v}$  (see end of Section 4). This identification is, however, invalid when the potential energy is not negligible and one has to add to  $f(\mathbf{r}, \mathbf{v})$  also information about the energy density. This is discussed in detail in [2]. Boltzmann's famous  $H$ -theorem derived from his eponymous equation for dilute gases is thus an expression of the second law applied to the macrostate specified by  $f$ . It was also argued in [2] that such an  $H$ -theorem must hold whenever there is a deterministic equation for the macrovariables of an isolated system.

fixed macroscopic time period  $\tau$  occupies a subset of  $\Gamma_M$  whose Liouville volume is a fraction of  $|\Gamma_M|$  which goes very rapidly (exponentially) to one as the number of atoms in the system increases. The fraction of “bad” microstates, which lead to an entropy decrease, thus goes to zero as  $N \rightarrow \infty$ .

Typicality is what distinguishes macroscopic irreversibility from the weak approach to equilibrium of probability distributions (ensembles) of systems with good ergodic properties having only a few degrees of freedom, e.g. two hard spheres in a cubical box. While the former is manifested in a typical evolution of a single macroscopic system the latter does not correspond to any appearance of time asymmetry in the evolution of an individual system. Maxwell makes clear the importance of the separation between microscopic and macroscopic scales when he writes [22]: “the second law is drawn from our experience of bodies consisting of an immense number of molecules. ...it is continually being violated, ..., in any sufficiently small group of molecules .... As the number ...is increased ...the probability of a measurable variation ...may be regarded as practically an impossibility.” This is also made very clear by Onsager in [21] and should be contrasted with the confusing statements found in many books that thermodynamics can be applied to a single isolated particle in a box, cf. footnote 9.

On the other hand, because of the exponential increase of the phase space volume with particle number, even a system with only a few hundred particles, such as is commonly used in molecular dynamics computer simulations, will, when started in a nonequilibrium ‘macrostate’  $M$ , with ‘random’  $X \in \Gamma_M$ , appear to behave like a macroscopic system.<sup>5</sup> This will be so even when integer arithmetic is used in the simulations so that the system behaves as a truly isolated one; when its velocities are reversed the system retraces its steps until it comes back to the initial state (with reversed velocities), after which it again proceeds (up to very long Poincaré recurrence times) in the typical way, see Section 5 and Figures 2 and 3.

We might take as a summary of such insights in the late part of the nineteenth century the statement by Gibbs [25] quoted by Boltzmann (in a German translation) on the cover of his book *Lectures on Gas Theory II* ([7]): “In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability.”

## 2 The use of probabilities

As already noted, typical here means overwhelmingly probable with respect to a measure which assigns (at least approximately) equal weights to regions of equal phase space volume within  $\Gamma_M$  or, loosely speaking, to different microstates consistent with the “initial” macrostate  $M$ . (This is also what was meant earlier by the ‘random’ choice of an initial  $X \in \Gamma_M$  in the computer simulations.) In fact, any mathematical statement about probable or improbable behavior of a physical system has to refer to some agreed

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<sup>5</sup>After all, the likelihood of hitting, in the course of say one thousand tries, something which has probability of order  $2^{-N}$  is, for all practical purposes, the same, whether  $N$  is a hundred or  $10^{23}$ . Of course the fluctuation in  $S_B$  both along the path towards equilibrium and in equilibrium will be larger when  $N$  is small, cf. [2b].

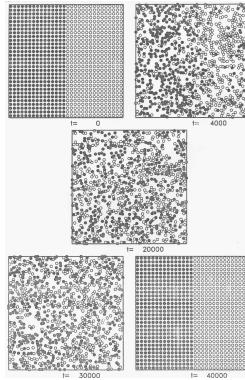


Figure 2. Time evolution of a system of 900 particles all interacting via the same cutoff Lennard-Jones pair potential using integer arithmetic. Half of the particles are colored white, the other half black. All velocities are reversed at  $t = 20,000$ . The system then retraces its path and the initial state is fully recovered. From Levesque and Verlet, see [23].

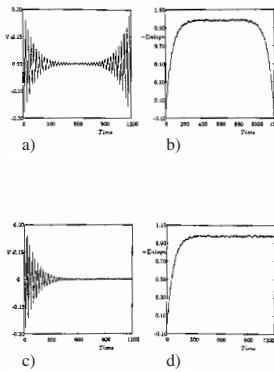


Figure 3. Time evolution of a reversible cellular automaton lattice gas using integer arithmetic. Figures a) and c) show the mean velocity, figures b) and d) the entropy. The mean velocity decays with time and the entropy increases up to  $t = 600$  when there is a reversal of all velocities. The system then retraces its path and the initial state is fully recovered in figures a) and b). In the bottom figures there is a small error in the reversal at  $t = 600$ . While such an error has no appreciable effect on the initial evolution it effectively prevents any recovery of the initial state. The entropy, on the scale of the figure, just remains at its maximum value. This shows the instability of the reversed path. From Nadiga et al. [24].

upon measure (probability distribution). It is, however, very hard (perhaps impossible) to formulate precisely what one means, as a statement about the real world, by an assignment of exact numerical values of probabilities (let alone rigorously justify any particular one) in our context. It is therefore not so surprising that this use of probabilities, and particularly the use of typicality for explaining the origin of the apparently

deterministic second law, was very difficult for many of Boltzmann's contemporaries, and even for some people today, to accept. (Many text books on statistical mechanics are unfortunately either silent or confusing on this very important point.) This was clearly very frustrating to Boltzmann as it is also to me, see [1b, 1c]. I have not found any better way of expressing this frustration than Boltzmann did when he wrote, in his second reply to Zermelo in 1897 [6] “The applicability of probability theory to a particular case cannot of course be proved rigorously. ...Despite this, every insurance company relies on probability theory. ...It is even more valid [here], on account of the huge number of molecules in a cubic millimetre...The assumption that these rare cases are not observed in nature is not strictly provable (nor is the entire mechanical picture itself) but in view of what has been said it is so natural and obvious, and so much in agreement with all experience with probabilities ...[that] ...*It is completely incomprehensible to me* [my italics] how anyone can see a refutation of the applicability of probability theory in the fact that some other argument shows that exceptions must occur now and then over a period of eons of time; for probability theory itself teaches just the same thing.”

The use of probabilities in the Maxwell–Thomson–Boltzmann explanation of irreversible macroscopic behavior is as Ruelle notes “simple but subtle” [14]. They introduce into the laws of nature notions of probability, which, certainly at that time, were quite alien to the scientific outlook. Physical laws were supposed to hold without any exceptions, not just almost always and indeed no exceptions were (or are) known to the second law as a statement about the actual behavior of isolated macroscopic systems; nor would we expect any, as Richard Feynman [15] rather conservatively says, “in a million years”. The reason for this, as already noted, is that for a macroscopic system the fraction (in terms of the Liouville volume) of the microstates in a macrostate  $M$  for which the evolution leads to macrostates  $M'$  with  $S_B(M') \geq S_B(M)$  is so close to one (in terms of their Liouville volume) that such behavior is exactly what should be seen to “always” happen. Thus in Figure 1 the sequence going from left to right is typical for a phase point in  $\Gamma_{M_a}$  while the one going from right to left has probability approaching zero with respect to a uniform distribution in  $\Gamma_{M_d}$ , when  $N$ , the number of particles (or degrees of freedom) in the system, is sufficiently large. The situation can be quite different when  $N$  is small as noted in the last section: see Maxwell quote there.

Note that Boltzmann's explanation of why  $S_B(M_t)$  is never seen to decrease with  $t$  does not really require the assumption that over very long periods of time a macroscopic system should be found in every region  $\Gamma_M$ , i.e. in every macroscopic states  $M$ , for a fraction of time *exactly* equal to the ratio of  $|\Gamma_M|$  to the total phase space volume specified by its energy. This latter behavior, embodied for example in Einstein's formula

$$\text{Prob}\{M\} \sim \exp[S_B(M) - S_{\text{eq}}] \quad (2)$$

for fluctuation in equilibrium systems, with probability there interpreted as the fraction of time which such a system will spend in  $\Gamma_M$ , can be considered as a mild form of the ergodic hypothesis, mild because it is only applied to those regions of the phase space representing macrostates  $\Gamma_M$ . This seems very plausible in the absence of constants of

the motion which decompose the energy surface into regions with different macroscopic states. It appears even more reasonable when we take into account the lack of perfect isolation in practice which will be discussed later. Its implication for small fluctuations from equilibrium is certainly consistent with observations. In particular when the exponent in (2) is expanded in a Taylor series and only quadratic terms are kept, we obtain a Gaussian distribution for normal (small) fluctuations from equilibrium. Equation (2) is in fact one of the main ingredients of Onsager's reciprocity relations for transport processes in systems close to equilibrium [26].

The usual ergodic hypothesis, i.e. that the fraction of time spent by a trajectory  $X_t$  in any region  $A$  on the energy surface  $H(X) = E$  is equal to the fraction of the volume occupied by  $A$ , also seems like a natural assumption for macroscopic systems. It is however not necessary for identifying equilibrium properties of macroscopic systems with those obtained from the microcanonical ensemble; see Section 7. Neither is it in any way sufficient for explaining the approach to equilibrium observed in real systems: the time scales are entirely different.

It should perhaps be emphasized again here that an important ingredient in the whole picture of the time evolution of macrostates described above is the constancy in time of the Liouville volume of sets in the phase space  $\Gamma$  as they evolve under the Hamiltonian dynamics (Liouville's theorem). Without this invariance the connection between phase space volume and probability would be impossible or at least very problematic.

For a somewhat different viewpoint on the issues discussed in this section the reader is referred to Chapter IV in [13].

### 3 Initial conditions

Once we accept the statistical explanation of why macroscopic systems evolve in a manner that makes  $S_B$  increase with time, there remains the nagging problem (of which Boltzmann was well aware) of what we mean by "with time": since the microscopic dynamical laws are symmetric, the two directions of the time variable are *a priori* equivalent and thus must remain so *a posteriori*. This was well expressed by Schrödinger [27]. "First, my good friend, you state that the two directions of your time variable, from  $-t$  to  $+t$  and from  $+t$  to  $-t$  are *a priori* equivalent. Then by fine arguments appealing to common sense you show that disorder (or 'entropy') must with overwhelming probability increase with time. Now, if you please, what do you mean by 'with time'? Do you mean in the direction  $-t$  to  $+t$ ? But if your interferences are sound, they are equally valid for the direction  $+t$  to  $-t$ . If these two directions are equivalent *a priori*, then they remain so *a posteriori*. The conclusions can never invalidate the premise. Then your inference is valid for both directions of time, and that is a contradiction."

In terms of our Figure 1 this question may be put as follows:<sup>6</sup> why can we use phase space arguments (or time asymmetric diffusion type equations) to predict the

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<sup>6</sup>The reader should think of Figure 1 as representing energy density in a solid: the darker the hotter. The time evolution of the macrostate will then be given by the heat (diffusion) equation.

macrostate at time  $t$  of an *isolated* system whose macrostate at time  $t_b$  is  $M_b$ , in the future, i.e. for  $t > t_b$ , but not in the past, i.e. for  $t < t_b$ ? After all, if the macrostate  $M$  is invariant under velocity reversal of all the atoms, then the same prediction should apply equally to  $t_b + \tau$  and  $t_b - \tau$ . A plausible answer to this question is to assume that the nonequilibrium macrostate  $M_b$  had its origin in an even more nonuniform macrostate  $M_a$ , prepared by some experimentalist at some earlier time  $t_a < t_b$  (as is indeed the case in Figure 1) and that for states thus prepared we can apply our (approximately) equal a priori probability of microstates argument, i.e. we can assume its validity at time  $t_a$ . But what about events on the sun or in a supernova explosion where there are no experimentalists? And what, for that matter, is so special about the status of the experimentalist? Isn't he or she part of the physical universe?

Before trying to answer these “big” questions let us consider whether the assignment of equal probabilities for  $X \in \Gamma_{M_a}$  at  $t_a$  permits the use of an equal probability distribution of  $X \in \Gamma_{M_b}$  at time  $t_b$  for predicting macrostates at times  $t > t_b > t_a$  when the system is isolated for  $t > t_a$ . Note that those microstates in  $\Gamma_{M_b}$  which have come from  $\Gamma_{M_a}$  through the time evolution during the time interval from  $t_a$  to  $t_b$  make up a set  $\Gamma_{ab}$  whose volume  $|\Gamma_{ab}|$  is by Liouville’s theorem at most equal<sup>7</sup> to  $|\Gamma_{M_a}|$ ; which, as already discussed before, is only a very small fraction of the volume of  $\Gamma_{M_b}$ . Thus we have to show that the overwhelming majority of phase points in  $\Gamma_{ab}$  (with respect to Liouville measure on  $\Gamma_{ab}$ ), have *future* macrostates like those typical of  $\Gamma_b$  – while still being very special and unrepresentative of  $\Gamma_{M_b}$  as far as their *past* macrostates are concerned. This property is explicitly proven by Lanford in his derivation of the Boltzmann equation (for short times) [17], and is part of the derivation of hydrodynamic equations [18], [19]; see also [28].

To see intuitively the origin of this property we note that for systems with realistic interactions the phase space region  $\Gamma_{ab} \subset \Gamma_{M_b}$  will be so convoluted as to *appear* uniformly smeared out in  $\Gamma_{M_b}$ . It is therefore reasonable that the future behavior of the system, as far as macrostates go, will be unaffected by their past history. It would of course be nice to prove this in all cases, “thus justifying” (for practical purposes) the factorization or “Stoßzahlansatz” assumed by Boltzmann in deriving his dilute gas kinetic equation for all times  $t > t_a$ , not only for the short times proven by Lanford [17]. However, our mathematical abilities are equal to this task only in very simple models such as the Lorentz gas in a Sinai billiard. This model describes the evolution of a macroscopic system of independent particles moving according to Newtonian dynamics in a periodic array of scatterers. For this system one can actually derive a diffusion equation for the macroscopic density profile  $n(\mathbf{r}, t)$  from the Hamiltonian dynamics [18]; see Section 8.

This behavior can also be seen explicitly in a many particle system, each of which

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<sup>7</sup>  $|\Gamma_{ab}|$  may be strictly less than  $|\Gamma_{M_a}|$  because some of the phase points in  $\Gamma_{M_a}$  may not go into  $\Gamma_{M_b}$ . There will be approximate equality when  $M_a$  at time  $t_a$ , determines  $M_b$  at time  $t_b$ : say via the diffusion equation for the energy density. This corresponds to the “Markov case” discussed in [13]. There are of course situations where the macrostate at time  $t$ , depends also (weakly or even strongly) on the whole history of  $M$  in some time interval prior to  $t$ , e.g. in materials with memory. The second law certainly holds also for these cases - with the appropriate definition of  $S_B$ , obtained in many case by just refining the description so that the new macro variables follow autonomous laws [13].

evolves independently according to the reversible and area preserving baker's transformation (which can be thought of as a toy version of the above case) see [29]. Here the phase space  $\Gamma$  for  $N$  particles is the  $2N$  dimensional unit hypercube, i.e.  $X$  corresponds to specifying  $N$ -points  $(x_1, y_1, \dots, x_N, y_N)$  in the unit square. The discrete time evolution is given by

$$(x_i, y_i) \rightarrow \begin{cases} (2x_i, \frac{1}{2}y_i), & 0 \leq x_i < \frac{1}{2} \\ (2x_i - 1, \frac{1}{2}y_i + \frac{1}{2}), & x_i \leq \frac{1}{2} < 1. \end{cases}$$

Dividing the unit square into  $4^k$  little squares  $\delta_\alpha$ ,  $\alpha = 1, \dots, K$ ,  $K = 4^k$ , of side lengths  $2^{-k}$ , we define the macrostate  $M$  by giving the fraction of particles  $p_\alpha = (N_\alpha/N)$  in each  $\delta_\alpha$  within some tolerance. The Boltzmann entropy is then given, using (1) and setting Boltzmann's constant equal to 1, by

$$S_B = \sum_{\alpha} \log \left[ \frac{\delta^{N_\alpha}}{N_\alpha!} \right] \simeq -N \sum_{\alpha} \left[ -1 + p(\alpha) \log \frac{p(\alpha)}{\delta} \right],$$

where  $p(\alpha) = N_\alpha/N$ ,  $\delta = |\delta_\alpha| = 4^{-k}$ , and we have used Stirling's formula appropriate for  $N_\alpha \gg 1$ . Letting now  $N \rightarrow \infty$ , followed by  $K \rightarrow \infty$  we obtain

$$N^{-1} S_B \rightarrow - \int_0^1 \int_0^1 \bar{f}(x, y) \log \bar{f}(x, y) dx dy + 1$$

where  $\bar{f}(x, y)$  is the smoothed density,  $p(\alpha) \sim \bar{f}\delta$ , which behaves according to the second law. In particular  $p_t(\alpha)$  will approach the equilibrium state corresponding to  $p_{eq}(\alpha) = 4^{-k}$  while the empirical density  $f_t$  will approach one in the unit square [29]. N.B. If we had considered instead the Gibbs entropy  $S_G$ ,  $N^{-1} S_G = - \int_0^1 \int_0^1 f_1 \log f_1 dx dy$ , with  $f_1(x, y)$  the marginal, i.e. reduced, one particle distribution, then this would not change with time. See Section 7 and [2].

## 4 Velocity reversal

The large number of atoms present in a macroscopic system plus the chaotic nature of the dynamics "of all realistic systems" also explains why it is so difficult, essentially impossible, for a clever experimentalist to deliberately put such a system in a microstate which will lead it to evolve in isolation, for any significant time  $\tau$ , in a way contrary to the second law.<sup>8</sup> Such microstates certainly exist – just reverse all velocities Figure 1b. In fact, they are readily created in the computer simulations with no round off errors, see Figures 2 and 3. To quote again from Thomson's article [4]: "If we allowed this equalization to proceed for a certain time, and then reversed the motions of all the molecules, we would observe a disequalization. However, if the number of molecules is very large, as it is in a gas, any slight deviation from absolute precision in the reversal

<sup>8</sup>I am not considering here entropy increase of the experimentalist and experimental apparatus directly associated with creating such a state.

will greatly shorten the time during which disequalization occurs.” It is to be expected that this time interval decreases with the increase of the chaoticity of the dynamics. In *addition*, if the system is not perfectly isolated, as is always the case for real systems, the effect of unavoidable small outside influences, which are unimportant for the evolution of macrostates in which  $|\Gamma_M|$  is increasing, will greatly destabilize evolution in the opposite direction when the trajectory has to *be aimed* at a very small region of the phase space.

The last statement is based on the very reasonable assumption that almost any small outside perturbation of an “untypical” microstate  $X \in \Gamma_{M(X)}$  will tend to change it to a microstate  $Y \in \Gamma_{M(X)}$  whose future time evolution is typical of  $\Gamma_{M(X)}$ , i.e.  $Y$  will likely be a typical point in  $\Gamma_{M(X)}$  so that typical behavior is not affected by the perturbation [14]. If however we are, as in Figure 1, in a micro-state  $X_b$  at time  $t_b$ , where  $X_b = T_\tau X_a$ ,  $\tau = t_b - t_a > 0$ , with  $|\Gamma_{M_b}| \gg |\Gamma_{M_a}|$ , and we now reverse all velocities, then  $RX_b$  will be heading towards a smaller phase space volume during the interval  $(t_b, t_b + \tau)$  and this behavior is very untypical of  $\Gamma_{M_b}$ . The velocity reversal therefore requires “perfect aiming” and will, as noted by Thomson [4], very likely be derailed by even small imperfections in the reversal and/or tiny outside influences. After a *very short* time interval  $\tau' \ll \tau$ , in which  $S_B$  decreases, the imperfections in the reversal and the “outside” perturbations, such as those coming from a sun flare, a star quake in a distant galaxy (a long time ago) or from a butterfly beating its wings [14], will make it increase again. This is clearly illustrated in Figure 3, which shows how a small perturbation has no effect on the forward macro evolution, but completely destroys the time reversed evolution.

The situation is somewhat analogous to those pinball machine type puzzles where one is supposed to get a small metal ball into a small hole. You have to do things just right to get it in but almost any vibration gets it out into larger regions. For the macroscopic systems we are considering, the disparity between relative sizes of the comparable regions in the phase space is unimaginably larger<sup>3</sup> than in the puzzle, as noted in the example in Section 1. In the absence of any “grand conspiracy”, the behavior of such systems can therefore be confidently predicted to be in accordance with the second law (except possibly for very short time intervals). This is the reason why even in those special cases such as spin-echo type experiments where the creation of an effective  $RT_\tau X$  is possible, the “anti-second law” trajectory lasts only for a short time [30]. In addition the *total* entropy change in the whole process, including that in the apparatus used to affect the spin reversal, is always positive in accord with the second law.

## 5 Cosmological considerations

Let us return now to the big question posed earlier: what is special about  $t_a$  in Figure 1 compared to  $t_b$  in a world with symmetric microscopic laws? Put differently, where ultimately do initial conditions, such as those assumed at  $t_a$ , come from? In thinking about this we are led more or less inevitably to introduce cosmological considerations

by postulating an initial “macrostate of the universe” having a very small Boltzmann entropy, (see also 1e and 1f). To again quote Boltzmann [31]: “That in nature the transition from a probable to an improbable state does not take place as often as the converse, can be explained by assuming a very improbable [small  $S_B$ ] initial state of the entire universe surrounding us. This is a reasonable assumption to make, since it enables us to explain the facts of experience, and one should not expect to be able to deduce it from anything more fundamental”. While this requires that the initial macrostate of the universe, call it  $M_0$ , be very far from equilibrium with  $|\Gamma_{M_0}| \ll |\Gamma_{M_{eq}}|$ , it does not require that we choose a special microstate in  $\Gamma_{M_0}$ . As also noted by Boltzmann elsewhere “we do not have to assume a special type of initial condition in order to give a mechanical proof of the second law, if we are willing to accept a statistical viewpoint...if the initial state is chosen at random...entropy is almost certain to increase.” This is a very important aspect of Boltzmann’s insight, it is sufficient to assume that this microstate is typical of an initial macrostate  $M_0$  which is far from equilibrium.

This going back to the initial conditions, i.e. the existence of an early state of the universe (presumably close to the big bang) with a much lower value of  $S_B$  than the present universe, as an ingredient in the explanation of the observed time asymmetric behavior, bothers some physicists.<sup>9</sup> It really shouldn’t since the initial state of the universe plus the dynamics determines what is happening at present. Conversely, we can deduce information about the initial state from what we observe now. As put by Feynman [15], “it is necessary to add to the physical laws the hypothesis that in the past the universe was more ordered, in the technical sense, [i.e. low  $S_B$ ] than it is today...to make an understanding of the irreversibility.” A very clear discussion of this is given by Roger Penrose in connection with the “big bang” cosmology [16]. He takes for the initial macrostate of the universe the smooth energy density state prevalent soon after the big bang: an equilibrium state (at a very high temperature) *except* for the gravitational degrees of freedom which were totally out of equilibrium, as evidenced by the fact that the matter-energy density was spatially very uniform. That such a uniform density corresponds to a nonequilibrium state may seem at first surprising, but gravity, being purely attractive and long range, is unlike any of the other fundamental forces. When there is enough matter/energy around, it completely overcomes the tendency towards uniformization observed in ordinary objects at high energy densities or temperatures. Hence, in a universe dominated, like ours, by gravity, a uniform density corresponds to a state of very low entropy, or phase space volume, for a given total energy, see Figure 4.

The local ‘order’ or low entropy we see around us (and elsewhere) – from complex molecules to trees to the brains of experimentalists preparing macrostates – is perfectly consistent with (and possibly even a necessary consequence of, i.e. typical of) this initial

---

<sup>9</sup>A common question is: how does the mixing of the two colors after removing the partitions in Figure 1 depend on the initial conditions of the universe. The answer is that once you accept that the microstate of the system in Figure 1a is typical of its macrostate the future evolution of the macrostates of this isolated system will indeed look like those depicted in Figure 1. It is the existence of inks of different colors separated in different compartments by an experimentalist, indeed the very existence of the solar system, etc. which depends on the initial conditions. In a “typical” universe everything would be in equilibrium.

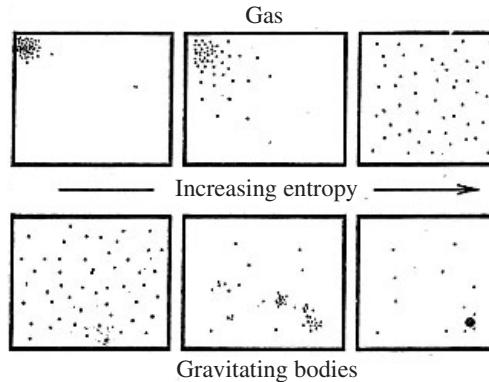


Figure 4. With a gas in a box, the maximum entropy state (thermal equilibrium) has the gas distributed uniformly; however, with a system of gravitating bodies, entropy can be increased from the uniform state by gravitational clumping leading eventually to a black hole. From [16].

macrostate of the universe. The value of  $S_B$  at the present time,  $t_p$ , corresponding to  $S_B(M_{t_p})$  of our current clumpy macrostate describing a universe of planets, stars, galaxies, and black holes, is much much larger than  $S_B(M_0)$ , the Boltzmann entropy of the “initial state”, but still quite far away from  $S_B(M_{eq})$  its equilibrium value. The ‘natural’ or ‘equilibrium’ state of the universe,  $M_{eq}$ , is, according to Penrose [16], one with all matter and energy collapsed into one big black hole. Penrose gives an estimate  $S_B(M_0)/S_B(M_{t_p})/S_{eq} \sim 10^{88}/10^{101}/10^{123}$  in natural (Planck) units, see Figure 5. (So we may still have a long way to go.)

I find Penrose’s consideration about the very far from equilibrium uniform density initial state quite plausible, but it is obviously far from proven. In any case it is, as Feynman says, both necessary and sufficient to assume a far from equilibrium initial state of the universe, and this is in accord with all cosmological evidence. The question as to why the universe started out in such a very unusual low entropy initial state worries Penrose quite a lot (since it is not explained by any current theory) but such a state is just accepted as a given by Boltzmann. My own feelings are in between. It would certainly be nice to have a theory which would explain the “cosmological initial state” but I am not holding my breath. Of course, if one believes in the “anthropic principle” in which there are many universes and ours just happens to be right or we would not be here then there is no problem – but I don’t find this very convincing [32].

## 6 Boltzmann vs. Gibbs entropies

The Boltzmannian approach, which focuses on the evolution of a single macroscopic system, is conceptually different from what is commonly referred to as the Gibbsian approach, which focuses primarily on probability distributions or ensembles. This difference shows up strikingly when we compare Boltzmann’s entropy – defined in

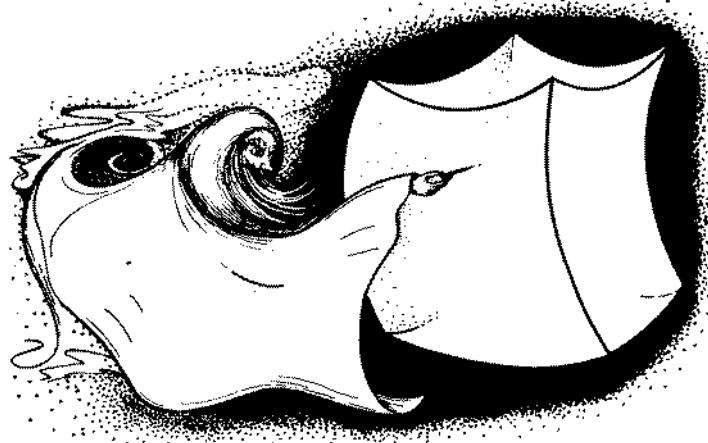


Figure 5. The creator locating the tiny region of phase-space – one part in  $10^{10^{123}}$  – needed to produce a  $10^{80}$ -baryon closed universe with a second law of thermodynamics in the form we know it. From ref. [16]. If the initial state was chosen randomly it would, with overwhelming probability, have led to a universe in a state with maximal entropy. In such a universe there would be no stars, planets, people or a second law.

(1) for a microstate  $X$  of a macroscopic system – with the more commonly used (and misused) entropy  $S_G$  of Gibbs, defined for an ensemble density  $\rho(X)$  by

$$S_G(\{\rho\}) = -k \int \rho(X) [\log \rho(X)] dX. \quad (3)$$

Here  $\rho(X)dX$  is the probability (obtained some way or other) for the microscopic state of the system to be found in the phase space volume element  $dX$  and the integral is over the phase space  $\Gamma$ . Of course if we take  $\rho(X)$  to be the generalized microcanonical ensemble associated with a macrostate  $M$ ,

$$\rho_M(X) \equiv \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M, \\ 0, & \text{otherwise,} \end{cases} \quad (4)$$

then clearly

$$S_G(\{\rho_M\}) = k \log |\Gamma_M| = S_B(M). \quad (5)$$

The probability density  $\rho_{M_{eq}}$  for a system in the equilibrium macrostate  $M_{eq}$  is, as already noted, essentially the same as that for the microcanonical (and equivalent also to the canonical or grandcanonical) ensemble when the system is of macroscopic size. Generalized microcanonical ensembles  $\rho_M(X)$ , or their canonical versions, are also often used to describe systems in which the particle density, energy density and momentum density vary slowly on a microscopic scale *and* the system is, in each small macroscopic region, in equilibrium with the prescribed local densities, i.e. in which

we have local equilibrium [18]. In such cases  $S_G(\{\rho_M\})$  and  $S_B(M)$  agree with each other, and with the macroscopic hydrodynamic entropy, to leading order in system size<sup>4</sup>. (The  $\rho_M$  do not however describe the fluxes in such systems: the average of  $J(X)$ , the microscopic flux function, being zero for  $\rho_M$  [18].)

The time evolutions of  $S_B$  and  $S_G$  subsequent to some initial time when  $\rho = \rho_M$  are very different, unless  $M = M_{\text{eq}}$  when there is no further systematic change in  $M$  or  $\rho$ . As is well known, it follows from the fact (Liouville's theorem) that the volume of phase space regions remains unchanged under the Hamiltonian time evolution (even though their shape changes greatly) that  $S_G(\{\rho\})$  never changes in time as long as  $X$  evolves according to the Hamiltonian evolution, i.e.  $\rho$  evolves according to the Liouville equation.  $S_B(M)$ , on the other hand, certainly does change. Thus, if we consider the evolution of the microcanonical ensemble corresponding to the macrostate  $M_a$  in Figure 1a after removal of the constraint,  $S_G$  would equal  $S_B$  initially but subsequently  $S_B$  would increase while  $S_G$  would remain constant.  $S_G$  therefore does not give any indication that the system is evolving towards equilibrium.

This reflects the fact, discussed earlier, that the probability density  $\rho_t(X)$  does not remain uniform over the domain corresponding to the macrostate  $M_t = M(X_t)$  for  $t > 0$ . I am thinking here of the case in which  $M_t$  evolves deterministically so that almost all  $X$  initially in  $\Gamma_{M_0}$  will be in  $\Gamma_{M_t}$  at time  $t$ , cf. [2]. As long as the system remains truly isolated  $\rho_t(X)$  will contain memories of the initial  $\rho_0$  in the higher order correlations, which are reflected in the complicated shape which an initial region  $\Gamma_{M_0}$  takes on in time but which do not affect the future time evolution of  $M$  (see the discussion at end of Section 4). *Thus the relevant entropy for understanding the time evolution of macroscopic systems is  $S_B$  and not  $S_G$ .*

Of course, if we do, at each time  $t$ , a “coarse graining” of  $\rho$  over the cell  $\Gamma_{M_t}$  then we are essentially back to dealing with  $\rho_{M_t}$ , and we are just defining  $S_B$  in a backhanded way. This is one of the standard ways, used in many textbooks, of reconciling the constancy of  $S_G$  with the behavior of the entropy in real systems. I fail to see what is gained by this except to obscure the fact that the microstate of a system is specified at any instant of time by a single phase point  $X_t$  and that its evolution in time is totally independent of how well we know the actual value of  $X_t$ . Why not use  $S_B$  from the beginning? We can of course still use ensembles for computations. They will yield correct results whenever the quantities measured, which may involve averages over some time interval  $\tau$ , have small dispersion in the ensemble considered.

## 7 Quantitative macroscopic evolution

Let me now describe briefly the very important but very daunting task of actually rigorously deriving time asymmetric hydrodynamic equations from reversible microscopic laws [18], [19]. While many qualitative features of irreversible macroscopic behavior depend very little on the positivity of Lyapunov exponents, ergodicity, or mixing properties of the microscopic dynamics, such properties are important for the existence of a quantitative description of the macroscopic evolution via time-asymmetric *autonomous*

equations of hydrodynamic type. The existence and form of such equations depend on the rapid decay of correlations in space and time, which requires chaotic dynamics. When the chaoticity can be proven to be strong enough (and of the right form) such equations can be derived rigorously from the reversible microscopic dynamics by taking limits in which the ratio of macroscopic to microscopic scales goes to infinity. Using the law of large numbers one shows that these equations describe the behavior of almost all individual systems in the ensemble, not just that of ensemble averages, i.e. that the dispersion goes to zero in the scaling limit. The equations also hold, to a high accuracy, when the macro/micro ratio is finite but very large [18].

As already mentioned, an example in which this can be worked out in detail is the periodic Lorentz gas. This consists of a *macroscopic number of non-interacting particles* moving among a periodic array of fixed convex scatterers, arranged in the plane in such a way that there is a maximum distance a particle can travel between collisions (finite horizon Sinai billiard). The chaotic nature of the microscopic dynamics, which leads on microscopic time scales to an approximately isotropic local distribution of velocities, is directly responsible for the existence of a simple autonomous deterministic description, via a diffusion equation, for the macroscopic particle density profile of this system [18]. A second example is a system of hard spheres at very low densities for which the Boltzmann equation has been shown to describe (at least for short times) [17] the evolution of  $f_t(\mathbf{r}, \mathbf{v})$ , the empirical density in the six dimensional position and velocity space. I use these examples, despite their highly idealized nature, because here (and unfortunately only here) all the mathematical i's have been dotted. They thus show *ipso facto*, in a way that should convince even (as Mark Kac put it) an "unreasonable" person, not only that there is no conflict between reversible microscopic and irreversible macroscopic behavior but also that, in these cases at least, *for almost all initial microscopic states consistent with a given nonequilibrium macroscopic state*, the latter follows from the former – in complete accord with Boltzmann's ideas.

## 8 Quantum mechanics

While the above analysis was done, following Maxwell, Thomson and Boltzmann, in terms of classical mechanics, the situation is in many ways similar in quantum mechanics. Formally the reversible incompressible flow in phase space is replaced by the unitary evolution of wave functions in Hilbert space and velocity reversal of  $X$  by complex conjugation of the wavefunction  $\Psi$ . In particular, I do not believe that quantum *measurement* is a *new* source of irreversibility. Rather, real measurements on quantum systems are time-asymmetric because they involve, of necessity, systems with a very large number of degrees of freedom whose irreversibility can be understood using natural extensions of classical ideas [33]. There are however also some genuinely new features in quantum mechanics relevant to our problem; for a more complete discussion see [34].

**Similarities.** Let me begin with the similarities. The analogue of the Gibbs entropy of an ensemble, equation (3), is the well known von Neumann entropy of a density matrix  $\hat{\mu}$ ,

$$\hat{S}_{vN}(\hat{\mu}) = -k \operatorname{Tr} \hat{\mu} \log \hat{\mu}. \quad (6)$$

This entropy, like the classical  $S_G(\rho)$ , does not change in time for an isolated system evolving under the Schrödinger time evolution [13], [35]. Furthermore it has the value zero whenever  $\hat{\mu}$  represents a pure state. It is thus, like  $S_G(\rho)$ , not appropriate for describing the time asymmetric behavior of an isolated macroscopic system. We therefore naturally look for the analog of the Boltzmann entropy given by equation (1). We shall see that while the quantum version of (1b) is straight forward there is no strict analog of (1a) with  $X$  replaced by  $\Psi$  which holds for all  $\Psi$ .

In a surprisingly little quoted part of his famous book on quantum mechanics [35], von Neumann discusses what he calls the macroscopic entropy of a system. To begin with, von Neumann describes a macrostate  $M$  of a macroscopic quantum system<sup>10</sup> by specifying the values of a set of “rounded off” commuting macroscopic observables, i.e. operators  $\hat{M}$ , representing particle number, energy, etc., in each of the cells into which the box containing the system is divided (within some tolerance). Labeling the set of eigenvalues of the  $\hat{M}$  by  $M_\alpha$ ,  $\alpha = 1, \dots$ , one then has, corresponding to the collection  $\{M_\alpha\}$ , an orthogonal decomposition of the system’s Hilbert space  $\mathcal{H}$  into linear subspaces  $\hat{\Gamma}_\alpha$  in which the observables  $\hat{M}$  take the values of  $M_\alpha$ . (We use here the subscript  $\alpha$  to avoid confusion with the operators  $\hat{M}$ .)

Calling  $E_\alpha$  the projection into  $\hat{\Gamma}_\alpha$ , von Neumann then defines the *macroscopic entropy* of a system with a density matrix;  $\hat{\mu}$  as,

$$\hat{S}_{\text{mac}}(\hat{\mu}) = k \sum_{\alpha=1}^L p_\alpha(\hat{\mu}) \log |\hat{\Gamma}_\alpha| - k \sum_{\alpha=1}^L p_\alpha(\hat{\mu}) \log p_\alpha(\hat{\mu}) \quad (7)$$

where  $p_\alpha(\hat{\mu})$  is the probability of finding the system with density matrix  $\hat{\mu}$  in the macrostate  $M_\alpha$ ,

$$p_\alpha(\hat{\mu}) = \operatorname{Tr}(E_\alpha \hat{\mu}), \quad (8)$$

and  $|\hat{\Gamma}_\alpha|$  is the dimension of  $\hat{\Gamma}_\alpha$  (equation (6) is at the bottom of p. 411 in [35]; see also equation (4) in [36]). An entirely analogous definition is made for a system represented by a wavefunction  $\Psi$ : we simply replace  $p_\alpha(\hat{\mu})$  in (7) and (8) by  $p_\alpha(\Psi) = (\Psi, E_\alpha \Psi)$ . In fact  $|\Psi\rangle\langle\Psi|$  just corresponds, as is well known, to a particular (*pure*) density matrix  $\hat{\mu}$ .

Von Neumann justifies (7) by noting that

$$\hat{S}_{\text{mac}}(\hat{\mu}) = -k \operatorname{Tr}[\tilde{\mu} \log \tilde{\mu}] = S_{vN}(\tilde{\mu}) \quad (9)$$

for

$$\tilde{\mu} = \sum (p_\alpha / |\hat{\Gamma}_\alpha|) E_\alpha \quad (10)$$

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<sup>10</sup>von Neumann unfortunately does not always make a clear distinction between systems of macroscopic size and those consisting of only a few particles and this leads I believe to much confusion, cf. article by Kemble [36]. See also articles by Bocchieri and Loinger [37], who say it correctly.

and that  $\tilde{\mu}$  is macroscopically indistinguishable from  $\hat{\mu}$ . This is analogous to the classical “coarse graining” discussed at the end of Section 7, with  $\tilde{\mu}_\alpha = E_\alpha / |\hat{\Gamma}_\alpha| \leftrightarrow \rho_{M_\alpha}$  there.

It seems natural to make the correspondence between the partitioning of classical phase space  $\Gamma$  and the decomposition of the Hilbert space  $\mathcal{H}$  and to define the natural quantum analogue to Boltzmann’s definition of  $S_B(M)$  in (1), as

$$\hat{S}_B(M_\alpha) = k \log |\hat{\Gamma}_{M_\alpha}| \quad (11)$$

where  $|\hat{\Gamma}_M|$  is the dimension of  $\hat{\Gamma}_M$ . This is in fact done more or less explicitly in [35], [37], [13], [38] and is clearly consistent with the standard prescription for computing the von Neumann quantum entropy of an equilibrium systems, with  $\hat{\mu} = \hat{\mu}_{\text{eq}}$ , where  $\hat{\mu}_{\text{eq}}$  is the microcanonical density matrix;  $\hat{\mu}_{\text{eq}} \sim \tilde{\mu}_\alpha$ , corresponding to  $M_\alpha = M_{\text{eq}}$ . This was in fact probably standard at one time but since forgotten. In this case the right side of (11) is, to leading order in the size of the system, equal to the von Neumann entropy computed from the microcanonical density matrix (*as it is for classical systems*) [13].

With this definition of  $\hat{S}_B(M)$ , the first term on the right side of equation (7) is just what we would intuitively write down for the expected value of the entropy of a classical system of whose macrostate we were unsure, e.g. if we saw a pot of water on the burner and made some guess, described by the probability distribution  $p_\alpha$ , about its temperature or energy. The second term in (7) will be negligible compared to the first term for a macroscopic system, classical or quantum, going to zero when divided by the number of particles in the system.

One can give arguments for expecting  $\hat{S}_B(M_t)$  to increase (or stay constant) with  $t$  after a constraint is lifted in a macroscopic system until the system reaches the macrostate  $M_{\text{eq}}$  [38], [37], [34]. These arguments are on the heuristic conceptual level analogous to those given above for classical systems, although there are at present no worked out examples analogous to those described in the last section. This will hopefully be remedied in the near future.

**Differences.** We come now to the differences between the classical and quantum pictures. While in the classical case the actual state of the system is described by  $X \in \Gamma_\alpha$ , for some  $\alpha$ , so that the system is always definitely in one of the macrostates  $M_\alpha$ , this is not so for a quantum system specified by  $\hat{\mu}$  or  $\Psi$ . We thus do not have the analog of (1a) for general  $\hat{\mu}$  or  $\Psi$ . In fact, even when the system is in a microstate  $\hat{\mu}$  or  $\Psi$  corresponding to a definite macrostate at time  $t_0$ , only a classical system will always be in a unique macrostate for all times  $t$ . The quantum system may evolve to a superposition of different macrostates, as happens in the well known Schrödinger cat paradox: a wave function  $\Psi$  corresponding to a particular macrostate evolves into a linear combination of wavefunctions associated with very different macrostates, one corresponding to a live and one to a dead cat (see references [38]–[41]).

The possibility of superposition of wavefunctions is of course a general, one might say the central, feature of quantum mechanics. It is reflected here by the fact that whereas the relevant classical phase space can be partitioned into cells  $\Gamma_M$  such that

every  $X$  belongs to exactly one cell, i.e. every microstate corresponds to a unique macrostate, this is not so in quantum mechanics. The superposition principle rules out any such meaningful partition of the Hilbert space: all we have is an orthogonal decomposition. Thus one cannot associate a definite macroscopic state to an arbitrary wave function of the system. This in turn raises questions about the connection between the quantum formalism and our picture of reality, questions which are very much part of the fundamental issues concerning the interpretation of quantum mechanics as a theory of events in the real world; see [16], and [38]–[44] and references there for a discussion of these problems.

Another related difference between classical and quantum mechanics is that quantum correlations between separated systems arising from wave function entanglement render very problematic, in general, our assigning a wave function to a subsystem  $\mathcal{S}_1$  of a system  $\mathcal{S}$  consisting of parts  $\mathcal{S}_1$ , and  $\mathcal{S}_2$  even when there is no direct interaction between  $\mathcal{S}_1$  and  $\mathcal{S}_2$ . This makes the standard idealization of physics – an isolated system – much more problematical in quantum mechanics than in classical theory. In fact any system, considered as a subsystem of the universe described by some wavefunction  $\Psi$ , will in general not be described by a wavefunction but by a density matrix,  $\mu^\Psi = \text{Tr}|\Psi><\Psi|$  where the trace is over  $\mathcal{S}_2$ .

It turns out that for a small system coupled to a large system, which may be considered as a heat bath, the density matrix of the small system will be the canonical one,  $\hat{\mu}_s = \hat{\mu}_\beta \sim \exp[-\beta \hat{H}_s]$  [45], [46]. To be more precise, assume that the (small) system plus heat bath ( $s + B$ ) are described by a microcanonical ensemble, specified by giving a uniform distribution over all normalized wave functions  $\Psi$  of  $(s + B)$  in an energy shell  $(E, E + \delta E)$ . Then the reduced density matrix of the system  $\hat{\mu}_s = \text{Tr}_B|\Psi><\Psi|$  obtained from any typical  $\Psi$  will be close to  $\hat{\mu}_\beta$ , i.e. the difference between them will go to zero (in the trace norm) as the number of degrees of freedom in the bath goes to infinity. This is a remarkable property of quantum systems which has no classical analogue. All one can say classically is that if one averages over the microstates of the bath one gets the canonical Gibbs distribution for the system. This is of course also true and well known for quantum systems, but what is new is that this is actually true for almost all pure states  $\Psi$ , [45], [46] see also references there to earlier work in that direction, including [37].

One can even go further and find the distribution of the “wave function”  $\varphi$  of the small system described by  $\hat{\mu}_\beta$  [47]. For ways of giving meaning to the wavefunction of a subsystem, see [41]–[42] and [48].

## 9 Final remarks

As I stated in the beginning, I have here completely ignored relativity, special or general. The phenomenon we wish to explain, namely the time-asymmetric behavior of macroscopic objects, has certainly many aspects which are the same in the relativistic (real) universe as in a (model) non-relativistic one. The situation is of course very different when we consider the entropy of black holes and the nature of the appropriate initial

cosmological state where relativity is crucial. Similarly the questions about the nature of time mentioned in the beginning of this article cannot be discussed meaningfully without relativity. Such considerations may yet lead to entirely different pictures of the nature of reality and may shed light on the interpretation of quantum mechanics, discussed in the last section, cf. [16]. Still it is my belief that one can and in fact one must, in order to make any scientific progress, isolate segments of reality for separate analysis. It is only after the individual parts are understood, on their own terms, that one can hope to synthesize a *complete picture*.

To conclude, I believe that the Maxwell–Thomson–Boltzmann resolution of the problem of the origin of macroscopic irreversibility contains, in the simplest idealized classical context, the essential ingredients for understanding this phenomena in real systems. Abandoning Boltzmann’s insights would, as Schrödinger says<sup>11</sup> be a most serious scientific regression. I have yet to see any good reason to doubt Schrödinger’s assessment.

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<sup>11</sup>Schrödinger writes [26], “the spontaneous transition from order to disorder is the quintessence of Boltzmann’s theory ... This theory really grants an understanding and does not ... reason away the dissymmetry of things by means of an a priori sense of direction of time variables ... No one who has once understood Boltzmann’s theory will ever again have recourse to such expedients. It would be a scientific regression beside which a repudiation of Copernicus in favor of Ptolemy would seem trifling.”

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Josef Stefan (1835–1893)  
(Courtesy of the Österreichische Zentralbibliothek für Physik)

# What physical quantities make sense in nonequilibrium statistical mechanics?

David Ruelle

## Introduction

Statistical mechanics, as seen by Boltzmann, is an attempt to understand the bulk properties of matter in terms of the dynamics of its microscopic constituents. The bulk properties of matter are described at the macroscopic level by thermodynamics.

**Thermodynamics: equilibrium and nonequilibrium.** Equilibrium thermodynamics is based on the observation that some states of matter, the equilibrium states, are operationally definable. One can associate with equilibrium states some quantities, notably temperature and entropy, that are not part of macroscopic mechanics. In equilibrium “nothing happens” at the macroscopic level. In nonequilibrium thermodynamics “things happen”: heat is transferred, temperature may depend on spatial coordinate and on time. More importantly, the global entropy is not constant in time, it always increases. There is a great variety of nonequilibrium phenomena, including chemical reactions, and the so-called transport phenomena. We shall be especially interested in these transport phenomena, where a gradient of temperature (or concentration, or velocity in a fluid) produces a “transport” or flux of heat (or solute, or momentum). A quantity of particular interest is the entropy production rate (entropy produced per unit time per unit volume).

**Equilibrium statistical mechanics.** Maxwell, Boltzmann and Gibbs have understood that the equilibrium states of thermodynamics have a probabilistic description at the microscopic level. If  $H(\mathbf{p}, \mathbf{q})$  is the Hamiltonian depending on the momentum variables  $\mathbf{p} = (p_1, \dots, p_N)$  and configuration coordinates  $\mathbf{q} = (q_1, \dots, q_N)$ , the probability that  $\mathbf{p}, \mathbf{q}$  are microscopically realized is given by the “normalized Boltzmann factor”

$$P(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q} = \frac{1}{Q} \exp \left[ -\frac{1}{kT} H(\mathbf{p}, \mathbf{q}) \right] d\mathbf{p} d\mathbf{q}$$

where  $T$  is the absolute temperature, and  $k$  is Boltzmann’s constant. We shall use the “inverse temperature”  $\beta = 1/kT$  and take  $k = 1$ . The above probability distribution is known as the “canonical ensemble”, and one shows that it is in some sense equivalent to other “ensembles” in the limit of a large system (thermodynamic limit). We shall not go into details, but note that equilibrium statistical mechanics is an *emergent theory* with respect to Hamiltonian mechanics: it applies only to certain systems (like particles with short range interactions), certain states (equilibrium states), and introduces the new concept of absolute temperature. The concept of entropy can also be defined, it is

given by

$$-\int P(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q} \log P(\mathbf{p}, \mathbf{q})$$

(it is basically the logarithm of the volume of occupied phase space, *i.e.*, the part of  $(\mathbf{p}, \mathbf{q})$ -space where the probability of the system is somehow significant). A fundamental feature of the emergent theory of equilibrium statistical mechanics is that it ignores dynamics: time does not occur. Of course, if one tries to justify the ensembles of equilibrium statistical mechanics one will have to use dynamics, but once one has the ensembles, the theory proceeds without dynamics. Equilibrium statistical mechanics is conceptually simple, it has been an enormously successful physical theory, and has also led to beautiful mathematical developments.

**0.1 Nonequilibrium statistical mechanics close to equilibrium.** While Boltzmann is one of the fathers of equilibrium statistical mechanics, he is *the* father of nonequilibrium statistical mechanics. He has basically explained why entropy increases in nonequilibrium (see [14]). Here is the idea: Hamiltonian dynamics preserves phase space volume (Liouville's theorem) but different regions of phase space may be so finely mixed by the dynamics that they progressively become indistinguishable. The apparent entropy, which corresponds to the mixed volume is thus larger than the entropy corresponding to the volume of an initial region.

Nonequilibrium statistical mechanics is now relatively well understood close to equilibrium. This development, which took place around the middle of the 20th century, is linked to the names of Onsager, Green, Kubo, ... (see [4]). A great simplification that occurs close to equilibrium is that thermostats are not needed, and one can obtain transport coefficients by some kind of first order perturbation theory around equilibrium (linear response theory). It turns out that the transport coefficients (*i.e.*, diffusion coefficients, viscosity, ...) are given in terms of the well understood equilibrium states, and the microscopic dynamics in these states, *i.e.*, time correlation functions. Dynamics appears thus here, but in a limited way.

Note that chemical reactions are not “close to equilibrium” in the sense needed for the above ideas to apply. Also, the mathematical justification of linear response theory is still unsatisfactory, because the microscopic dynamics in equilibrium states remains poorly understood. In fact, it seems that to make sense of linear response close to equilibrium requires understanding nonequilibrium statistical mechanics away from equilibrium (this is often called “far from equilibrium”, but “a finite distance away from equilibrium” is what is really meant).

## 1 Nonequilibrium statistical mechanics away from equilibrium

We shall concern ourselves here with transport phenomena and, more specifically, with heat transfer. We want thus to consider systems that are macroscopically described by a temperature field, but no density or velocity field. We have thus one macroscopically conserved quantity (energy, or heat), and no particles for which we would have to

consider conservation of particle number and perhaps of momentum. The fact is that the discussion of moving particles entails technical difficulties that we want to avoid. We shall in fact restrict ourselves to three classes of nonequilibrium systems for which the time evolution is mathematically well controlled. We present now our three classes.

**1.1 Systems with isokinetic thermostating [8], [11].** These are systems described by  $2N$  real variables:  $p_1, \dots, p_N, q_1, \dots, q_N$ , and we write  $\mathbf{p} = (p_1, \dots, p_N)$ ,  $\mathbf{q} = (q_1, \dots, q_N)$ .

**Case I.**

$$\frac{d}{dt} \begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix} = \begin{pmatrix} \xi(\mathbf{q}) - \alpha \mathbf{p} \\ \mathbf{p}/m \end{pmatrix}$$

where  $\alpha = \mathbf{p} \cdot \xi(\mathbf{q}) / \mathbf{p}^2$ . This differs from a Hamiltonian evolution equation by the fact that  $\xi$  need not be a gradient (*i.e.*, we need not have  $\xi = -\nabla_{\mathbf{q}} U(\mathbf{q})$ ), and that a term  $-\alpha \mathbf{p}$  has been added. We have

$$\frac{d}{dt} \frac{\mathbf{p}^2}{2m} = \frac{1}{m} \mathbf{p} \cdot \frac{d}{dt} \mathbf{p} = 0$$

*i.e.*, the kinetic energy does not change.

Note that a probability measure  $\rho(\mathbf{x}) d\mathbf{x}$  has a (Gibbs) entropy

$$S = - \int \rho(\mathbf{x}) d\mathbf{x} \log \rho(\mathbf{x}).$$

One finds quite generally, for the time evolution given by a vector field  $X$ , that

$$\frac{dS}{dt} = \int \rho(\mathbf{x}) d\mathbf{x} \operatorname{div} X = \int \rho(d\mathbf{x}) \operatorname{div} X$$

where the  $\operatorname{div}$  is with respect to  $d\mathbf{x}$ , and the right-hand side makes sense even if the measure  $\rho$  is singular. It is argued that the rate of creation of entropy by the system is  $-dS/dt$ : this is the entropy that the external world sees coming out of the system, while the entropy of the system tends to  $-\infty$ , and the measure describing it tends to a singular nonequilibrium steady state (NESS)  $\rho$ . The rate of entropy production can thus be identified to the rate of volume contraction in phase space [1]. In our case

$$-\operatorname{div} X = \nabla_{\mathbf{p}} \cdot (\alpha \mathbf{p}) = N\alpha + \mathbf{p} \cdot \nabla_{\mathbf{p}} \alpha = (N-1)\alpha.$$

We may write  $\alpha = w/2K$  where  $w = \mathbf{p} \cdot \xi(\mathbf{q})/m$  is the work per unit time performed by  $\xi$  and  $K = \mathbf{p}^2/2m$  is the kinetic energy, which is constant. We may associate with  $K$  a temperature  $\beta^{-1}$  such that  $K = (N-1)\beta^{-1}/2$  (equipartition of energy suggests a factor  $N$  rather than  $N-1$ , but remember that  $\mathbf{p}$  is constrained here to an  $N-1$  dimensional manifold). We may thus write

$$-\operatorname{div} X = (N-1)\alpha = \beta w$$

hence

$$\text{rate of entropy creation} = (N - 1) \int \alpha = \beta \int w$$

where the integral is taken with respect to the NESS: this is the usual thermodynamic relation.

**Case II.** Instead of thermostating all  $N$  degrees of freedom to temperature  $\beta^{-1}$  for a system with nongradient force  $\xi$ , we may also consider a Hamiltonian system where we fix the kinetic energy of a subsystem  $X_1$  with  $N_1$  degrees of freedom to a value  $K_1$ , and the kinetic energy of a subsystem  $X_2$  with  $N_2$  degrees of freedom to a value  $K_2$ . This means that we replace in the equation of motion  $\dot{\xi} - \alpha \mathbf{p}$  by  $\dot{\xi} - \alpha_1 \mathbf{p}_1 - \alpha_2 \mathbf{p}_2$  where we now take  $\xi = -\nabla_{\mathbf{q}} U(\mathbf{q})$ ,  $\alpha_1 = \xi \cdot \mathbf{p}_1 / \mathbf{p}_1^2$ ,  $\alpha_2 = \xi \cdot \mathbf{p}_2^2$  (we use the notation  $\mathbf{p}_1 = (p_i)_{i \in X_1}$  and  $\mathbf{p}_2 = (p_i)_{i \in X_2}$ ). We write  $\beta_1 = 2K_1/(N_1 - 1)$ ,  $\beta_2 = 2K_2/(N_2 - 1)$  and assume  $\beta_1^{-1} < \beta_2^{-1}$ . The energy per unit time received by the  $i$ th thermostat is  $w_i = \mathbf{p}_i \cdot \dot{\xi}(\mathbf{q})/m$ , and

$$\begin{aligned} -\text{div}X &= \nabla_{\mathbf{p}} \cdot (\alpha_1 \mathbf{p}_1 + \alpha_2 \mathbf{p}_2) \\ &= N_1 \alpha_1 + N_2 \alpha_2 + \mathbf{p}_1 \cdot \nabla_{\mathbf{p}_1} \alpha_1 + \mathbf{p}_2 \cdot \nabla_{\mathbf{p}_2} \alpha_2 \\ &= (N_1 - 1)\alpha_1 + (N_2 - 1)\alpha_2 \\ &= \beta_1 w_1 + \beta_2 w_2. \end{aligned}$$

Since the forces inside the system are Hamiltonian, assuming that the energy of the system remains bounded gives  $\int w_1 + \int w_2 = 0$ , where the integral is with respect to the NESS, hence

$$\text{rate of entropy creation} = (\beta_1 - \beta_2) \int w_1$$

which is the usual thermodynamic relation.

One can argue that, in both Case I and Case II, the average of  $-\text{div}X$  in the NESS is  $\geq 0$  (basically this is because the volume in phase space cannot indefinitely increase), and this gives the correct (positive) sign for  $\int w$  or  $\int w_1$ .

**1.2 Infinite systems of classical rotators [18].** Let  $L$  be a countable set and  $\Gamma$  a graph with vertex set  $L$ . For each  $x \in L$  we consider a “rotator” described by variables  $q_x \in \mathbb{T}$ ,  $p_x \in \mathbb{R}$  and with hamiltonian  $H_x = p_x^2/2m + U_x(q_x)$ . We couple these rotators by interaction potentials  $W_{\{x,y\}}(q_x, q_y)$  when  $\{x, y\} \in \Gamma$ . To obtain the Hamiltonian of the system in a finite region  $\Lambda$  we let  $\Gamma_\Lambda$  be the restriction of  $\Gamma$  to  $\Lambda$  and write

$$H_\Lambda = \sum_{x \in \Lambda} H_x + \sum_{\{x,y\} \in \Gamma_\Lambda} W_{\{x,y\}}(q_x, q_y).$$

We assume that the graph  $\Gamma$  is finite dimensional and that the  $U_x$ ,  $W_{\{x,y\}}$  and their derivatives are uniformly bounded (we omit here technical details). It is also allowed to introduce an “external” (nongradient) force  $\xi$  acting on a finite number of rotators

(corresponding to a finite set  $\Lambda_0 \subset L$ ). One can then prove an existence and uniqueness theorem for the time evolution ( $f^t$ ) of the infinite system of oscillators just described.

Let  $\ell$  denote a state, *i.e.*, a probability measure on the infinite dimensional phase space of our system, then the time-evolved state  $f^t\ell$  is defined for all  $t$  and one can take as nonequilibrium steady states the limits when  $T \rightarrow \infty$  of

$$\frac{1}{T} \int_0^T dt f^t \ell.$$

We choose as initial state  $\ell$  a Gibbs state, *i.e.*, a limit of  $Z_\Lambda^{-1} e^{-\tilde{H}_\Lambda}$  when the finite set  $\Lambda \subset L$  tends to  $L$ , with

$$\tilde{H}_\Lambda = \sum_{x \in \Lambda} \left( \frac{p_x^2}{2m} + \tilde{U}_x(q_x) \right) + \sum_{\{x,y\} \in \Gamma_\Lambda} W_{\{x,y\}}(q_x, q_y)$$

and  $Z_\Lambda^{-1}$  a normalization factor. If we take  $\tilde{H} = \beta H$  outside of a finite region, our initial state is at temperature  $\beta^{-1}$  (outside of the finite region). Another possibility is to take  $L = L_1 \sqcup L_2 \sqcup$  finite region, and arrange that the initial state  $\ell$  is at temperature  $\beta_1^{-1}$  in the infinite set  $L_1$ , and at temperature  $\beta_2^{-1}$  in the infinite set  $L_2$ . Given a finite set  $X \subset L$  the state  $f^t\ell$ , integrated over the variables  $p_x, q_x$  for  $x \notin X$  is of the form

$$\ell_X^t(\mathbf{p}_X, \mathbf{q}_X) d\mathbf{p}_X d\mathbf{q}_X$$

where  $\mathbf{p}_X = (p_x)_{x \in X}$ ,  $\mathbf{q}_X = (q_x)_{x \in X}$ , and  $\ell_X^t$  is a smooth function bounded by

$$C_1(t) e^{-C_2(t)\mathbf{p}^2}.$$

In particular, one can associate with  $X, t$  an entropy

$$S^t(X) = - \int d\mathbf{p}_X d\mathbf{q}_X \ell_X^t(\mathbf{p}_X, \mathbf{q}_X) \log \ell_X^t(\mathbf{p}_X, \mathbf{q}_X)$$

and also a conditional entropy

$$\check{S}^t(X) = \lim_{\Lambda \rightarrow \infty} (S^t(\Lambda) - S^t(\Lambda \setminus X)).$$

It is then a natural idea to try to define the rate of entropy production in  $X$  as the time average of  $-dS^t(X)/dt$  or  $-d\check{S}^t(X)/dt$ , *i.e.*,

$$e(X) = \lim_{T \rightarrow \infty} \frac{S^0(X) - S^T(X)}{T}, \quad \check{e}(X) = \lim_{T \rightarrow \infty} \frac{\check{S}^0(X) - \check{S}^T(X)}{T}$$

(the use of  $e(X)$  was proposed by Evans and coworkers [19], see also [9], [15]). We may again consider two cases.

**Case I.** There is an external force  $\xi$  and the system is thermostatted at temperature  $\beta^{-1}$ . Then

$$0 \leq e(X) \leq \check{e}(X) \leq \beta \times \text{energy flux from } \xi.$$

**Case II.** No external force, but two thermostats at temperatures  $\beta_1^{-1} < \beta_2^{-1}$ . Then

$$0 \leq e(X) \leq \check{e}(X) \leq (\beta_1 - \beta_2) \times \text{energy flux to thermostat 1}.$$

**1.3 Infinite quantum spin systems.** To each point  $x$  of a countably infinite set  $L$ , a finite dimensional Hilbert space  $\mathcal{H}_x$  is attached. For finite  $X \subset L$  we let  $\mathcal{A}_X$  be the algebra of bounded operators on  $\otimes_{x \in X} \mathcal{H}_x$ . With natural identifications, all the  $\mathcal{A}_X$  are subalgebras of a  $C^*$ -algebra  $\mathcal{A}$ , such that  $\bigcup_{X \text{ finite}} \mathcal{A}_X$  is norm-dense in  $\mathcal{A}$ . Choosing a self-adjoint  $\Phi(X) \in \mathcal{A}_X$  for each  $X$ , we define a formal Hamiltonian

$$H = \sum_X \Phi(X).$$

Under reasonable assumptions on the  $\|\Phi(X)\|$ , Robinson [3] has shown that  $H$  defines a time evolution, in the sense of a one-dimensional parameter group of  $*$ -automorphisms  $\alpha^t$  of the algebra  $\mathcal{A}$ . One writes  $L = L_1 \sqcup L_2 \sqcup$  finite region and one introduces, as initial state, a state  $\sigma$  on  $\mathcal{A}$  (= normalized positive linear form) describing equilibrium at temperature  $\beta_1^{-1}$  in the infinite set  $L_1$  and equilibrium at temperature  $\beta_2^{-1}$  in the infinite set  $L_2$ . By a compactness argument, one can let  $T$  tend to  $+\infty$  in such a way that the limits

$$\lim \frac{1}{T} \int_0^T dt \sigma(\alpha^t A) = \rho(A)$$

exist, defining a nonequilibrium steady state  $\rho$ . It can be proved [16], [12] that the thermodynamic expression for the entropy production is nonnegative:

$$(\beta_1 - \beta_2) \times \text{energy flux to thermostat } 1 \geq 0.$$

## 2 A study of physical quantities

We have considered three classes of systems which may describe nonequilibrium: (1) finite systems with IK thermostatting, (2) infinite systems of classical rotators, (3) infinite quantum spin systems. For the classes (1), (2) we could have an external force + thermostat (Case I). For the classes (1)–(3) we could have two thermostats at different temperatures (Case II). We shall now discuss which physical quantities can be associated with different types of systems.

In all the cases considered, the time evolution ( $(f^t)$  for (1),(2),  $(\alpha^t)$  for (3)) is well defined. For the class (1), the IK thermostatting is part of the equations of motion, and we can take a somewhat arbitrary initial condition  $\ell(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q}$  with  $\ell$  continuous decreasing fast as  $\mathbf{p} \rightarrow \infty$ . For the classes (2), (3), the thermostatting is part of the initial condition  $\ell$  or  $\sigma$ . By compactness, we may choose  $T \rightarrow \infty$  so that these time averages tend (in a weak sense) to a state  $\rho$ . This state is invariant under time evolution and we call  $\rho$  a nonequilibrium steady state (NESS). Note that for the class (1) (IK thermostatting), the NESS  $\rho$  is expected to be a singular measure, this is because we want nontrivial entropy production

$$e = \lim_{T \rightarrow \infty} \frac{S^0 - S^T}{T} > 0.$$

This implies  $S^T \rightarrow -\infty$ , hence  $f^T \ell \rightarrow$  singular. Note however, that if  $X \subset \{1, \dots, N\}$  is sufficiently small, the projection  $\rho_X$  of the NESS to  $X$  might be absolutely continuous. Similarly, for Class (2) systems, the  $\rho_X$  for finite  $X$  may be absolutely continuous.

**2.1 Temperature.** A priori, the temperature of the thermostats is well defined. For infinite thermostats (Classes (2), (3)) this should be physically the temperature far inside the thermostats. But note that we must require that the thermostats have dimension  $\geq 3$ . Indeed, if we consider a macroscopic continuous description of our system, it would have a temperature distribution satisfying the heat equation, and an asymptotically constant value of the temperature at infinity is not possible in dimensions 1 and 2.

For systems locally close to equilibrium, one could define a local temperature, but in general a local temperature would not seem to make much physical sense, because the local velocity distribution cannot be expected to be Maxwellian.

One might want to conjecture that, for a system with two thermostats at temperatures  $\beta_1^{-1} < \beta_2^{-1}$ , any reasonably defined local temperature  $\tilde{\beta}^{-1}$  would satisfy  $\beta_1 > \tilde{\beta} > \beta_2$ . Let me argue that this is incorrect. Indeed, we may imagine that our system contains a little green man (or woman) who, seeing a warm and a cold source, uses them to power an engine, and then either warms or cools some part of the system outside of the range  $[\beta_1^{-1}, \beta_2^{-1}]$ . In view of this remark we require, for Class (2) systems, that for each finite  $X$  the energy of the subsystem  $X$  is bounded independently of time. Note that this requirement could be violated in Case I if the thermostat had dimension  $< 3$ , because the energy produced by the external force could not be evacuated at the rate at which it is produced.

**2.2 Entropy.** The total entropy is expected to diverge for an infinite system. We shall thus try to give a meaning to the entropy of a finite set  $X$  in the NESS  $\rho$ . We shall discuss the Gibbs entropy  $S_\rho(X)$  because other definitions of entropy require a system close in some sense to equilibrium (see [14]). For Class (1) systems (IK thermostatted), we expect the NESS  $\rho$  to be singular, hence  $S_\rho(\{1, \dots, N\}) = -\infty$ . Of course if  $\rho$  is an equilibrium state  $S_\rho(\{1, \dots, N\})$  is finite, and one can try to extend the definition away from the equilibrium states [17], but this can be done consistently only close to equilibrium. For sufficiently small  $X \subset \{1, \dots, N\}$ , it appears possible that  $S_\rho(X)$  is finite. For Class (2) systems, it is believable that the projection  $\rho_X$  of the NESS to the finite region  $X$  is absolutely continuous and with finite entropy (see [5], [6], [2]), at least if  $X$  is disjoint from the region where an external force  $\xi$  is acting (Case I). For Class (3) systems (quantum spins), the von Neumann entropy  $S_\rho(X) = -\text{tr} \rho_X \log \rho_X$  is always finite. It would remain to discuss the possible use and physical meaning of  $S_\rho(X)$  when this quantity is finite.

**2.3 Global entropy production.** There is a thermodynamic formula for the global entropy production rate  $e$ . In Case I we have

$$e = \beta \times \text{energy flux from } \xi.$$

In Case II

$$e = (\beta_1 - \beta_2) \times \text{energy flux to thermostat 1}$$

and one has  $e \geq 0$ . This result, to be proved for each class of systems considered, is non trivial, it means that the energy flows in the “right” direction.

For systems with an IK thermostat we can also express the rate of entropy production in terms of phase space volume contraction, and this has led to the important fluctuation theorems [7], [10].

**2.4 Local entropy production.** For infinite classical Hamiltonian systems (our class (2)) Evans and coworkers [19] have proposed to define the rate of entropy production in a finite region  $X$  as the time average of  $-dS^t(X)/dt$ , *i.e.*,

$$e(X) = \lim_{T \rightarrow \infty} \frac{S^0(X) - S^T(X)}{T}.$$

This quantity is  $\geq 0$  but it is nontrivial, *i.e.*,  $e(X) > 0$ , only if  $S^T(X) \rightarrow \infty$  when  $T \rightarrow \infty$ . So, we cannot have both a finite entropy  $S_\rho(X)$  and a nontrivial entropy production  $e(X) > 0$ . The current evidence [5], [6], [2] is that the projection  $\rho_X$  of the NESS  $\rho$  to a finite region  $X$  is absolutely continuous (at least if  $X$  is disjoint from the region where an external force  $\xi$  is acting) and that  $e(X) = 0$ . It does not appear impossible at this time that  $\check{e}(X)$  (which is  $\geq e(X)$ ) yields a nontrivial definition of entropy production in the region  $X$ . (Note also that  $\check{e}(X)$  is a subadditive function of  $X$ , while  $e(X)$  is superadditive). The problem, however, is wide open. For the class (3) (quantum spin systems) we have  $\check{e}(X) = e(X) = 0$  because  $\check{S}^T(X)$  and  $S^T(X)$  are bounded.

### 3 Discussion

Let us again stress that our discussion of nonequilibrium has been restricted to transport (in fact heat transport), disregarding chemical reactions, metastability, etc. Also, we have focussed on nonequilibrium steady states, and ignored transient phenomena.

Boltzmann had a clear physical idea of why entropy increases in nonequilibrium processes. He was able to implement this idea for gas dynamics (the  $H$ -theorem) by ignoring recollisions, and this has led to a rigorous result (Lanford [13]). A rigorous mathematical formulation of entropy production is also possible when an IK thermostat is used. Unfortunately, it remains unclear if a local entropy production  $\check{e}(X)$  can be defined nontrivially for infinite classical systems. (For quantum spin systems, the evidence is that such a definition is not possible.)

The importance of identifying physical quantities in models of nonequilibrium is shown by the extraordinary success of the Fluctuation Theorem, based on the use of the IK thermostat and the identification of entropy production with volume contraction in phase space. The possibility of identifying a nontrivial local entropy production in infinite systems remains an important challenge. Perhaps progress on this question may

be obtained by numerical studies of subsystems of finite systems with IK thermostats and an external force (as indicated in [19]).

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Ludwig Boltzmann in Graz 1884  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)

# Boltzmann, ergodic theory, and chaos

Donald S. Ornstein

## Part A

Boltzmann's legacy for ergodic theory has two parts. The first comes from his realization that Newton's laws, by themselves, are an inadequate description of dynamics and that a probabilistic element must be added to include the arrow of time or the increase of entropy.

The second, his entropy theory came into ergodic theory much later, through the work of Shannon and Kolmogorov.

We can view a dynamical system driven by Newton's laws of motion as follows: We represent the state of the system as a point in the space of all states (the phase space, which we will denote by  $M$ ). Newton's laws determine how the point moves. We denote this flow by  $(F_t, M)$ .  $x$  at time 0 goes to  $F_t(x)$  at time  $t$ .

Boltzmann realized that, to prove that entropy increases, he needed to add a probability structure (Newton's laws are reversible). This invariant measure (probability) is supplied by Liouville's theorem. We denote this model by  $(F_t, M, u)$ .

This measure provides the structure needed for ergodic theory. We can think of it as a probability measure on the initial conditions of our system.

Probability (randomness) can also enter in another way. Because of the large number of atoms, we usually model a gas by a system where the time evolution itself (the mechanism driving the system) has a random element (we will refer to this as a random system).

It is, therefore, relevant to ask: To what extent can a system evolving according to Newton's laws be modeled by a random system? This is also the central question in chaos "theory".

This question has a more precise meaning in light of Kolmogorov's formulation of Boltzmann's model: Kolmogorov views the phase space,  $M, u$ , as an abstract measure space  $(X, u)$ , together with a function  $P$  on  $X$  that identifies  $X$  with  $M$  (we denote this model by  $(F_t, X, u, P)$ ).

This formulation puts random processes and Newtonian systems into the same mathematical framework, in the following way.

Kolmogorov's model for a stationary process is also a measure preserving flow on an abstract measure space,  $X$ , together with a function  $P$  on  $X$ ,  $(F_t, X, u, P)$ . The points in  $X$  are the doubly infinite sample paths of our process. The measure  $u$  comes from the probability of cylinder sets and the Kolmogorov extension theorem.  $F_t$  shifts the sample paths.  $P$  allows us to recover the sample paths as  $P(F_t(x))$ . Note that in this model no two points in  $X$  give the same sample path.

Kolmogorov then asked which  $(F_t, X, u)$  come from Newtonian (or smooth) systems, and which come from random systems. We will now examine two concrete systems and (hopefully) clarify our previous discussion.

**1. A Newtonian system.** The ball moves at constant speed and bounces off the sides and the obstacles, angle of incidence equaling the angle of reflection.

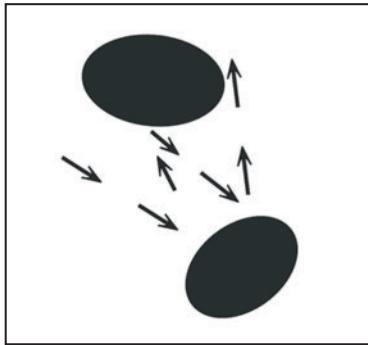


Figure 1

The phase space,  $M$ , is the unit tangent bundle to the table (position and direction) and the invariant measure is the three-dimension Lebesque measure. (We will denote this model by  $(\bar{F}_t, \bar{X}, \bar{u}, \bar{P})$ .)

## 2. A random model

**Markov flow.** For each  $N$  we define a Markov flow. Start with  $N$  points,  $np_i$ , on the table. Our process stays at  $np_i$  for time  $Nt_i$  and then flips a fair coin to decide which of a pair of points (determined by  $np_i$ ) to jump to.

We will denote this model by  $(\hat{F}_t, \hat{X}_t, \hat{u}, {}_N\hat{P})$ .

**Theorem.** *There is one  $B_t$ ,  $X$ ,  $u$ ,  $P$ ,<sup>1</sup> and a sequence  ${}_N\hat{P}$ , such that*

$$\begin{aligned} (B_t, X, u, P) &= (\bar{F}_t, \bar{X}, \bar{u}, \bar{P}) = \text{Sinai billiards}, \\ (B_t, X, u, {}_N P) &= (\hat{F}_t, \hat{X}_t, \hat{u}, {}_N \hat{P}) = \text{Markov flow}, \\ {}_N P &\rightarrow P \text{ in the } L_1 \text{ norm}. \end{aligned}$$

${}_N P$  can be defined by a partition of  $X$  (or  $M$ ) into a finite number of atoms and a point,  $np_i$ , in each atom. We can think of  ${}_N P$  as a coarse graining of  $M$ . We get the model for our Markov flow by viewing billiards through this course graining.

We would like to be able to use any sequence of course graining, but this is clearly impossible. However, we can use any sequence of course grainings with an arbitrary small modification. That is, we can start with any sequence of partitions,  ${}_N Q$  that,

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<sup>1</sup>  $F_t$  stands for a generic flow, whereas  $B_t$  stands for a specific  $F_t$ .

in the limit, separate points. (We could assume that the sup of the diameters,  $d$ , the  $|NQ_i - NP_i| \rightarrow 0$ .) We can choose any  $\varepsilon_N \rightarrow 0$  and insist that  $|NQ_i - NP_i| < \varepsilon_N$ .

Our model for billiards does not take into account our inability to make measurements of infinite accuracy. By adding a sequence of course grainings, we get a model where we can see the ball with arbitrarily good, but finite, accuracy. In this model, the distinction between a system evolving according to Newton's laws and one evolving by coin flipping disappears.

Another justification for modifying our Newtonian model by course graining is that Boltzmann's introduction of  $u$  does not completely explain the arrow of time. We need to take into account our ability to start our system in a set,  $E$ , of very small probability (all the gas in one half of the box) and our inability to start it in  $F_t(E)$  (because this set is spread out uniformly in the phase space).

These special starting sets correspond to some sort of course graining.

Another justification comes from chaos "theory". This "theory" is a collection of results that center on the observation that some Newtonian systems, even very simple ones, "appear" to be random.

The usual version is that some Newtonian systems are sensitive to initial conditions and, because we can't observe the initial conditions accurately (we only see the system through a course graining), the system is very unpredictable ("appears" to be random).

Our result says that, not only does Sinai billiards "appear" random, but, in a certain sense, it is random. When we look at billiards through a course graining, we see exactly a Markov flow.

## Part B

Our discussion seems to have wandered away from Boltzmann's legacy, but, in fact, it is based on Boltzmann's entropy, which was adapted by Shannon for stationary processes and, then, introduced into ergodic theory by Kolmogorov.

We will start our discussion with discrete time.

We call a measure preserving transformation on an abstract measure space  $(F, X, u)$  a Bernoulli shift (B-shift) if, for some  $P$ ,  $(F, X, u, P)$  is the model for an independent process.

One of the central, and oldest, questions in ergodic theory was: are all B-shifts the same? Kolmogorov answered this question by introducing entropy as an invariant for measure preserving transformations, and showed that if  $(F, X, u, P)$  is an independent process with probabilities  $p_i$ , then the entropy of  $(F, X, u)$  is  $\sum_i p_i \log p_i$  (thus, not all B-shifts are the same).

The next step was proving the converse: i.e., B-shifts with the same entropy are the same.

The Kolmogorov–Sinai introduction of entropy also organized the  $(F, X, u)$  into different levels of randomness.

At the bottom, there are the  $(F, X, u)$  of zero entropy. This is equivalent to: for any finite-valued  $P$ , the sample path from 0 to  $-\infty$  determines the output at all future

times. We think of these  $(F, X, u)$  as not really random.

On the other end, we have the Kolmogorov transformations (K-automorphisms) where there is no finite-valued  $P$  such that  $F, X, u, P$  has zero entropy (is predictable).

The K-automorphisms include the B-shifts.

It was once believed that the only K-automorphisms were the B-shifts, but this is not true and the K-automorphisms are a large class that includes uncountably many of the same entropy; some have no square root; some are not the same as their inverse, etc.

It was also believed (the Pinsker conjecture) that every transformation was the direct product of a zero entropy transformation and a K-automorphism. This is, again, false.

Returning to continuous time, we have the following isomorphism theorem, whose proof depends heavily on entropy.

(1) Every B-shift can be embedded in a flow (there is a flow,  $B_t$ , such that, for some  $t_0$ , the discrete time transformation,  $B_{t_0}$ , is the B-shift.

(2) There are only two such flows, one of finite and one of infinite entropy. (The finite entropy flow is unique, up to a constant rescaling of time, i.e., change the unit of time). We denote these by  $B_t$  and  $B_t^\infty$ .

(3) All of the discrete time transformations,  $B_{t_0}$  (and  $B_{t_0}^\infty$ ) are B-shifts.

(4) All of the B-shifts are realized by fixing some  $t_0$  in  $B_t$  or  $B_t^\infty$  (so they are really not so different after all).

(5) The only factors of  $B_t$  are  $B_t$  (possibly rescaled). (The factors of  $B_t^\infty$  are  $B_t$  or  $B_t^\infty$ .)

(6)  $B_t$  (or  $B_t^\infty$ ) is a full entropy factor of any  $F_t$  of non-zero entropy.

(5) and (6) need a little explaining. For  $(F_t, X, u, P)$  it could happen that more than one  $x$  in  $X$  gives the same sample path  $P(F_t(x))$ . This is the model for a stationary process only after we have lumped these  $x$  together. This lumping gives an invariant sub- $\sigma$ -algebra and  $F_t$  restricted to an invariant sub- $\sigma$ -algebra is called a factor.

An important implication of the isomorphism theorem is that, at the level of abstraction of measure preserving flows on abstract measure spaces  $(F_t, X, u)$  there is a unique flow that is the most random possible (really two flows,  $B_t$  and  $B_t^\infty$ .)

This is justified by the feeling that independent processes are the most random. Furthermore, if we think of  $P$  as a measurement on  $(F_t, X, u)$ , then (6) implies that if  $F_t$  has non-zero entropy, then any measurement on  $F_t$  will also occur as a measurement on  $B_t$  (or  $B_t^\infty$ ). Furthermore, if  $F$  is not  $B_t$  (or  $B_t^\infty$ ), then it will have measurements that do not appear as measurements on  $B_t$  (or  $B_t^\infty$ ).

Furthermore, if  $(F_t, X, u, P)$ , is a stationary process, where  $F_t$  is not  $B_t$  (or  $B_t^\infty$ ), then this process cannot be approximated arbitrarily well (even in the  $\bar{d}$  series) by a Markov flow.

Part of the isomorphism theorem that we did not describe are criteria for proving a system to be Bernoulli.

Applying one of these criteria, and using some hard results of Sinai, it was proved in that Sinai billiards are modeled by  $B_t$ .

Another criterion shows that the Markov flows are modeled by  $B_t$  (in particular, the Markov flow where we flip back and forth between just two points.)

There is a long list of systems that are modeled by  $B_t$  or  $B_t^\infty$ , but we will give just one more example<sup>2</sup>. Any SRB measure is modeled by  $B_t$ .

We built our discussion around Sinai billiards, but we could have used any flow on a Riemannian manifold that preserves a smooth measure and which can be proved to be Bernoulli (modeled by  $(B_t, X, u, P)$ ).

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<sup>2</sup>Because I think it the most relevant to the kinds of things that might have interested Boltzmann.

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The Boltzmann family in Graz 1886  
Children (left to right): Henriette, Ida Katherina, Ludwig Hugo, Arthur  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)



Ludwig Boltzmann in Graz 1887

Standing (left to right): Walther Nernst, Franz Streintz, Svante Arrhenius,  
Richard Hiecke; sitting (from left): Eduard Aulinger, Albert von Ettingshausen,  
Ludwig Boltzmann, Ignaz Klemencic, Viktor Hausmanninger

(Courtesy of the Österreichische Zentralbibliothek für Physik)

# 134 years of Boltzmann equation

Carlo Cercignani

## 1 The first 100 years

In 1872 [1] Boltzmann obtained the equation that bears his name and proved what later was called the *H*-theorem. Before writing his great paper, Boltzmann had learned to master Maxwell's techniques [2]. In fact, already in 1868 he had extended Maxwell's distribution to the case when the molecules are in equilibrium in a force field with potential [3], including the case of polyatomic molecules as well [4]. The energy equipartition theorem was also extended by him to the case of polyatomic molecules [5]. Boltzmann interprets the distribution function in two ways, which he seems to consider as *a priori* equivalent: the first one is to think of it as the fraction of a time interval sufficiently long, during which the velocity of a specific molecule has values within a certain volume element in velocity space, whereas the second (quoted in a footnote to paper [3]) is based on the fraction of molecules, which, at a given time instant, have a velocity in the said volume element. It seems clear, as remarked by Klein [6], that Boltzmann did not feel, at that time, any need to analyse the equivalence, implicitly assumed, between these two meanings, which are so different. He soon realized, however, (in a footnote to paper [5]) that it was necessary to make an assumption, "not improbable" for real bodies made of molecules that are moving because they possess "the motion that we call heat". This assumption, according to which the coordinates and the velocities of the molecules take on, in an equilibrium state, all values compatible with the assigned total energy of the gas, became later familiar with the name of ergodic hypothesis, given to it by Paul and Tatiana Ehrenfest [7].

Before discussing the basic paper of 1872 and the subsequent evolution of our understanding of the Boltzmann equation, we remark that in 1871 Boltzmann felt ready for a new attempt to understand the Second Law [8], starting from the equilibrium law that he had obtained in his previous papers and illustrating the difference between heat and work. He equated, as he had done previously and was common after the work of Clausius and Maxwell, something, that he denoted by  $T$  and called temperature, to the average of kinetic energy per atom (hence without using the so-called Boltzmann constant, which was introduced by Planck much later). We stress the fact that this identification, apart from a factor, is easily justified only if there is a proportionality between thermal energy and temperature; this is the case for perfect gases and solids at room temperature. The concept of temperature is indeed rather subtle, because it does not have a direct dynamic meaning. In a more modern perspective, the concept of entropy, introduced by Boltzmann in kinetic theory (together with thermal energy) appears more basic (though admittedly less intuitive) and temperature appears as a restricted concept, strictly meaningful for equilibrium states only.

The problems we have alluded to do not enter in the case considered by Boltzmann and we can accept his identification without objections. It is then clear that the total

energy  $E$ , sum of the kinetic and potential energies, will have the following average value:

$$\langle E \rangle = NT + \langle \chi \rangle \quad (1)$$

where  $\chi$  is the potential energy and  $\langle q \rangle$  denotes the average of a quantity  $q$  whereas  $N$  is the total number of molecules. It is then clear that one can change the value of  $\langle E \rangle$  in two ways, *i.e.* by changing either the temperature or the potential, so slowly as to go through equilibrium states, to obtain

$$\delta\langle E \rangle = N\delta T + \delta\langle \chi \rangle \quad (2)$$

where  $\delta$  (rather than the more typical  $d$ ) denotes an infinitesimal change. If we denote the heat supplied to the system in the process by  $\delta^* Q$  and compute it as the difference between the increase of average total energy and the average work done on the system, we have:

$$\delta^* Q = \delta\langle E \rangle - \langle \delta\chi \rangle = N\delta T + \delta\langle \chi \rangle - \langle \delta\chi \rangle. \quad (3)$$

We remark that  $\delta\langle \chi \rangle$  (the change of the average value of  $\chi$ ) and  $\langle \delta\chi \rangle$  (the average of the change of the value of  $\chi$ ) are different because the averages will depend on certain macroscopic parameters, typically temperature, which are allowed to change in the process under consideration.

The expression in equation (3) is not the differential of some state function  $Q$ , a circumstance underlined here by the presence of a star superscript affecting the symbol  $\delta$ . Boltzmann showed, however, that, if we divide the expression under consideration by  $T$ , one obtains the exact differential of a function, which he, of course, identified with entropy. He also proceeded to computing it explicitly for a perfect gas and for a simple model of a solid body, thus finding, in the first case, a result well known in thermodynamics, in the second an expression, from which he easily succeeded in obtaining the Dulong–Petit formula, empirically known for specific heats of most solids near room temperature.

Even if somebody acquainted with the usual thermodynamic calculations may find it a bit strange that the work performed on the system is due to the change in the potential rather than to the motion of a piston, the derivation by Boltzmann is impeccable, if one grants that the equilibrium distribution is what is called nowadays Maxwell–Boltzmann, and is now more or less standard. It was, however, a treatment that excluded irreversible phenomena and it could not have been otherwise since the said distribution holds only for equilibrium states.

But Boltzmann was by then ready for the last step, *i.e.* the extension of the statistical treatment to irreversible phenomena, on the basis of a new integrodifferential equation, which bears his name. As soon as he was sure of this result, he wanted to publish a short paper on Poggendorff's *Annalen* in order to ensure his priority in this discovery and to subsequently elaborate the results in a complete form for the Academy of Vienna. Since Stefan was against publishing twice the same material, we are left with just the memoir of almost 100 pages presented to the Academy [1]. This may explain the strange title, "Further researches on the thermal equilibrium of gas molecules", chosen to present a wealth of new results.

The paper started with a critique to the derivation of velocity distribution in a gas in an equilibrium state, given by Maxwell [2], with an emphasis on the fact that the said deduction had only shown that the Maxwellian distribution, once achieved, is not altered by collisions. However, said Boltzmann, “it has still not yet been proved that, whatever the initial state of the gas may be, it must always approach the limit found by Maxwell” [1]. When writing this statement Boltzmann had obviously in mind the spatially homogeneous case, to which the first part of the memoir is actually devoted.

On the basis of an “exact treatment of the collision processes”, he obtained an equation for the distribution function, usually denoted by  $f$ , *i.e.* the probability density of finding a molecule at a certain position  $x$  with a certain velocity  $\xi$  at some time instant  $t$ .

In the first part of the memoir he restricted himself to the case when  $f$  depends just on time and kinetic energy. This equation may appear a bit strange to the eyes of those who have in mind the version of the same equation which can be found in more recent treatments, not only because of the use of the letter  $x$  to denote kinetic energy. In fact the circumstance that he adopts this variable as an independent variable instead of velocity introduces several square roots in the equation; these are due to the fact that the volume element whose measure does not change with time during the evolution of the system, thanks to Liouville’s theorem, contains the volume element in velocity space  $d\xi_1 d\xi_2 d\xi_3$ . When transforming the variables in polar coordinates one obtains, in addition to the solid angle element, the element  $|\xi|^2 d|\xi|$  or, in terms of the kinetic energy  $E_{\text{kin}}$  and apart from constant factors,  $(E_{\text{kin}})^{1/2} dE_{\text{kin}}$ .

By means of his equation, Boltzmann showed not only that the Maxwell distribution is a steady solution of the equation, but that no other such solution can be found. This goal is achieved by introducing a quantity, that turns out to be, apart from a constant factor, the opposite of the entropy; the possibility of expressing the entropy in terms of the distribution function, though in a certain sense not unexpected, does not cease to stand as a remarkable fact, that must have produced a deep impression on Boltzmann’s contemporaries. In fact, as remarked by the author himself, it implied an entirely different approach to the proof of the Second Law, that showed not only the existence of an entropy function for the equilibrium states, but also permitted to study its increase in irreversible processes.

The paper goes on with an alternative derivation based on a model with discrete energies, in such a way that the integrodifferential equation for the distribution function becomes a system of ordinary nonlinear differential equations. The use of discrete energies has always appeared “much clearer and intuitive” [1] to Boltzmann. This statement may sound like a naïvety, but might also indicate a surprising intuition about the difficulties of a rigorous proof of the trend to equilibrium, which disappear if one has to deal with a discrete, finite system of equations, since the unknown  $f$  is, at any time instant, a finite set of numbers, instead of a function (we are dealing with a finite-dimensional space, rather than with a function space); this simplification permits to make use of a property, already known in Boltzmann’s days (the so-called Bolzano–Weierstrass theorem) in order to deduce the trend under consideration without particularly refined mathematical arguments. Many historians of science have underlined the circumstance

that these discrete models used by Boltzmann led Planck to the discovery of his energy *quanta*, as Planck himself acknowledged [9].

Just a few pages of the voluminous memoir by Boltzmann concern the calculation of the transport properties in a gas. It is in these pages, however, that Boltzmann laid down his equation in the most familiar form for us, where the distribution function depends upon time  $t$ , upon velocity  $\xi$  and upon position  $x$  (the vector notation is, of course, anachronistic). His calculations show that the viscosity, heat conduction and diffusion coefficients can be computed by means of his equation with results identical with those of Maxwell, for the so called Maxwellian molecules. Boltzmann, however, warned his readers against the illusion of an easy extension of his calculations to the case of more complicated interaction laws.

In order to explain Boltzmann's contributions in this exceptionally important paper, we shall start from this last part. We shall use an approach anachronistic not only because of the notation but also because of the argument we shall use. In fact, otherwise, it does not appear to be possible to treat the subject in an understandable and short form.

We shall imagine, unless we say otherwise, the molecules as hard, elastic and perfectly smooth spheres. Not only this choice will simplify our presentation, but it is also in a reasonable agreement with experience. Using more refined models would quantitatively improve this agreement, but would introduce several technical complications, without changing anything from a conceptual standpoint.

In order to discuss the behavior of a system of  $N$  (identical) hard spheres, it is very convenient to introduce the  $6N$ -dimensional phase space, where the Cartesian coordinates are the  $3N$  components of the  $N$  position vectors of the sphere centers  $x_i$  and the  $3N$  components of the  $N$  velocities  $\xi_i$ . Thus, if we have one molecule, we need a six-dimensional space, if we have two molecules we need twelve dimensions, etc. In this space, the state of the system, if known with absolute accuracy, is represented by a point having given values of the aforementioned coordinates. If the state is not known with absolute accuracy, we must introduce a probability density  $f(x, \xi, t)$  which gives the distribution of probability in phase space. Given  $f_0$ , the value of  $f$  at  $t = 0$ , we can compute  $f$  for  $t > 0$ , provided we have an equation giving its time evolution. Assuming that body forces (such as gravity) are omitted (for the sake of simplicity), Boltzmann wrote this equation in the form

$$\frac{df}{dt} = G - L. \quad (4)$$

Here  $df/dt$  is the partial derivative with respect to time in the space homogeneous case, but is, in general, the time derivative along the molecule's trajectory:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial x}. \quad (5)$$

$L dx d\xi dt$  gives the expected number of particles with position between  $x$  and  $x + dx$  and velocity between  $\xi$  and  $\xi + d\xi$  which disappear from these ranges of values because of a collision in the time interval between  $t$  and  $t + dt$  and  $G dx d\xi dt$  gives the analogous number of particles entering the same range in the same time interval. The count of

these numbers is not particularly difficult, provided we use the trick of imagining one molecule as a sphere at rest and endowed with twice the actual diameter  $\sigma$  and the other particles to be point masses with velocity  $(\xi_i - \xi) = V_i$ , where  $\xi$  is the velocity of the molecule that is considered at rest for the purpose of the count. In fact, each collision will send molecule 1 out of the above sets and the number of its collisions will be the number of expected collisions of any other point mass with that sphere. Since there are exactly  $(N - 1)$  identical point masses and multiple collisions are disregarded,  $G = (N - 1)g$  and  $L = (N - 1)l$ , where the lower case letters indicate the contribution of a fixed particle, say particle 2. For the details of the computation of  $g$  and  $l$ , see [10] and [11].

At this point we are ready to understand Boltzmann's argument in a heuristic way; a rigorous derivation (for short times only) was provided, as we shall discuss below, one hundred years later by O. Lanford [12]. In a gas, even if rarefied,  $N$  is still a huge number and  $\sigma$  (expressed in units suitable for objects that we handle in everyday life, such as, e.g., centimeters) is very small; to fix the ideas, let us consider a box whose volume is clearly visible, say  $1 \text{ cm}^3$ , at room temperature and atmospheric pressure. Then  $N \cong 10^{20}$  and  $\sigma = 10^{-8} \text{ cm}$ . Hence  $(N - 1)\sigma^2 \cong N\sigma^2 = 10^4 \text{ cm}^2 = 1 \text{ m}^2$  is a sizable quantity, while we can neglect the difference between  $\mathbf{x}$  and  $\mathbf{x} + \sigma\mathbf{n}$ , where  $\mathbf{n}$  is the unit vector directed as  $\mathbf{x}_* - \mathbf{x}$  (at the instant when the collision occurs, the magnitude of the latter vector is obviously equal to the molecular diameter  $\sigma$ ). This leads us to think that the equation to be written can be rigorously valid only in the so-called *Boltzmann-Grad limit*, when  $N \rightarrow \infty$ ,  $\sigma \rightarrow 0$  with  $N\sigma^2$  finite. Although one must credit Harold Grad [13], [14] with having first stated this idea in a precise mathematical form, it is clear that Boltzmann had in mind something similar. We quote, in fact, two passages from his lectures on gas theory:

“...the distribution law for molecular velocities is not precisely correct as long as the number of molecules is not mathematically infinite...” ([15], Volume 1, Section 6).

“In the molecular theory we assume that the laws of the phenomena found in nature do not essentially deviate from the limits that they approach in the case of infinite number of infinitesimally small molecules...If we accept this assumption, then we should also obtain agreement with experience by calculating the limit that the laws of the phenomena would approach in the case of an infinitely increasing number and decreasing size of the molecules...” ([15], Volume 2, Section 38).

Boltzmann was, of course, well aware of the fact that the number of particles per unit volume is finite in any real gas and that the size of the molecules is finite [15], Volume 1, Section 12; Volume 2, Section 22. The Boltzmann-Grad limit is a necessary condition for the Boltzmann equation to be rigorously valid; in some cases this has been proved also to be a sufficient condition with all mathematical rigor. From an intuitive standpoint, since, in our typical example above, the volume occupied by the molecules is about  $N\sigma^3 \cong 10^{-4} \text{ cm}^3$ , the collisions between two preselected molecules is a rather rare event. Thus two spheres that happen to collide can be thought to be two randomly chosen molecules. Hence it makes sense to assume that the probability density of finding the first molecule at  $\mathbf{x}$  with velocity  $\xi$  and the second at  $\mathbf{x}_*$  with velocity  $\xi_*$  is the product of the probability density of finding the first molecule at  $\mathbf{x}$  with velocity  $\xi$

times the probability density of finding the second molecule at  $\mathbf{x}_*$  with velocity  $\xi_*$ . This becomes correct only in the Boltzmann-Grad limit. Thus Boltzmann's cautious remarks are fully justified.

These considerations may be understood in a more general scheme excoitated to develop the following viewpoint: the fact that the continuum and molecular descriptions have a common ground of validity leads to the idea that we can elaborate a method permitting a rigorous deduction of the macroscopic equations starting from a microscopic model. The method is essentially based on the idea that the macroscopic behavior arises as a limiting one from the microscopic laws and is essentially due to the extremely large number of molecules coming into play.

This is part of a more general vision of our understanding of natural phenomena at various levels of description. The rougher descriptions correspond to phenomena that we meet in everyday life, but we must descend to lower layers in order to understand the reasons behind certain macroscopic behaviors and obtain more accurate laws.

If we accept the idea of statistical independence of two molecules with velocities  $\xi$  and  $\xi_*$  that happen to meet in a dilute gas, we can use the assumption of *molecular chaos* in the loss term but not to the gain term in the form, if this is expressed in terms of the post-collision velocities. It is possible, however, to express these in terms of the pre-collision velocities ( $\xi'$  and  $\xi'_*$ ).

If we accept all the simplifying assumptions made (more or less implicitly) by Boltzmann, we obtain, for the gain and loss terms  $G$  and  $L$ , expressions which contain  $f$  only:

$$\frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial \mathbf{x}} = N\sigma^2 \int_{\mathbb{R}^3} \int_{\mathbf{B}_-} [f(\mathbf{x}, \xi', t) f(\mathbf{x}, \xi'_*, t) - f(\mathbf{x}, \xi, t) f(\mathbf{x}, \xi_*, t)] |(\xi_* - \xi) \cdot \mathbf{n}| d\xi_* d\mathbf{n} \quad (6)$$

where  $\mathbf{n}$  is a unit vector and

$$\xi' = \xi - \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), \quad \xi'_* = \xi_* + \mathbf{n}(\mathbf{n} \cdot \mathbf{V}), \quad \mathbf{V} = \xi - \xi_*. \quad (7)$$

The Boltzmann equation is an evolution equation for  $f$  and this is its main advantage. It has been obtained, however, at the price of several assumptions; the chaos assumption is particularly strong and requires to be discussed a little bit. The main difficulty in this area is to distinguish between probabilistic and dynamic arguments; it is the use of probability, in fact, that makes the results acceptable and avoids the paradoxes that arise from a purely dynamic interpretation.

The molecular chaos is clearly a property of randomness. Intuitively, one feels that collisions exert a randomizing influence, and this can be made convincing with further considerations, but it would be completely wrong to argue that the statistical independence is a consequence of the dynamics (as Boltzmann seemed to maintain in his first papers on his equation). It is quite clear that we cannot expect every choice of the initial value for the many-particle distribution function  $f^{(N)}$  to give a one-particle distribution function  $f$  which agrees with the solution of the Boltzmann equation in the Boltzmann-Grad limit (since the Liouville equation is linear, half of the sum of

two initial data for  $P$ , each of which gives by assumption a  $f$  in agreement with the Boltzmann equation, would not be able to give the same agreement, since the Boltzmann equation is nonlinear). In other words molecular chaos must be present initially and we can only ask whether it is preserved by the time evolution of the system of hard spheres.

It is evident that the chaos property, *i.e.* absence of correlations, if initially present, is immediately destroyed, at least if we insist that it should be valid everywhere. In fact, if it were strictly valid at any point of phase space, the gain and loss terms, in the Boltzmann-Grad limit, would be exactly equal. Hence there would be no effect of the collisions on the time evolution of  $f$ . The essential point is that we need the chaos property only for molecules which are about to collide. It is clear, then, that even if  $f$ , as predicted by the Liouville equation, converges nicely (in the Boltzmann-Grad limit) to a solution of the Boltzmann equation, to the two-particle distribution function  $f^2$  may converge to a product only in a way, which is, in a certain sense, very singular. In fact, it is not enough to show that the convergence occurs for all points of phase space, *except those of a set of zero measure*, because we need to use the chaos property in a zero volume set (corresponding to the states of molecules which are about to collide). On the other hand we cannot try to show that convergence holds everywhere, because this would be false; in fact, we have just remarked that absence of correlations is, generally speaking, simply not true for molecules which have just collided.

How can we approach the question of justifying the Boltzmann equation without invoking the molecular chaos assumption as an *a priori* hypothesis? Obviously, since the two-particle distribution function  $f^2$  appears in the evolution equation for  $f$ , we must investigate the time evolution for  $f^{(2)}$ ; now, as is clear, and is illustrated in [10], [11], [16] the evolution equation for  $f^{(2)}$  contains the three-particle distribution function,  $f^{(3)}$ . In general if we introduce the so-called  $s$ -particle distribution function  $f^{(s)}$ , we find that the evolution equation of  $P^{(s)}$  contains the next function  $P^{(s+1)}$ , till we reach  $s = N$ ;  $f^{(N)}$  satisfies the Liouville equation. It is clear thus that we cannot proceed unless we handle all the  $f^{(s)}$  at the same time and attempt to prove a generalized form of molecular chaos, *i.e.*

$$f^{(s)}(\mathbf{x}, \xi, \mathbf{x}_*, \xi_*, \dots, \mathbf{x}_s, \xi_s, t) = \prod_{j=1}^s f(\mathbf{x}_j, \xi_j, t). \quad (8)$$

Thus the task becomes to show that, if true at  $t = 0$ , this property remains preserved (for any fixed  $s$ ) and for molecules about to collide, in the Boltzmann-Grad limit. This is discussed in detail in [12].

There remains the problem of justifying the *initial chaos assumption*, according to which the factorization holds at  $t = 0$ . One can give two justifications, one of them being physical in nature and the second mathematical; essentially, they say the same thing, *i.e.* that it is hard to prepare an initial state for which chaos does not hold. The physical reason for this is that, in general, we cannot handle the single molecules, but rather act on the gas as a whole, *i.e.* we act at a macroscopic level, usually starting from an equilibrium state (for which chaos holds). The mathematical argument indicates that, if we choose the initial data for the molecules at random there is an overwhelming probability [10], [11] that chaos is satisfied for  $t = 0$ .

This clarification, from a physical standpoint, is due to the Ehrenfests [7], while the problems posed by a mathematically rigorous justification are at the moment only partially solved.

A word should be said about boundary conditions, *i.e.* the conditions that the distribution function must satisfy at the points where the gas is bounded by a solid wall. When proving that chaos is preserved in the limit, it is absolutely necessary to have a boundary condition compatible (at least in the limit) with chaos. If the boundary conditions are those of periodicity in space or specular reflection, no problems arise. More in general, it is sufficient that the molecules are scattered without adsorption from the boundary in a way that does not depend on the state of the other molecules of the gas [10], [11].

It is appropriate here to comment upon Maxwell's transfer equations, which are very close to the Boltzmann equation, although there is no hint that Maxwell thought that they could be used to study the time evolution of the distribution function. In fact they can be written as follows:

$$\int_{\mathbb{R}^3} \frac{d}{dt} \phi(\xi) P^{(1)}(x, \xi, t) d\xi = \int_{\mathbb{R}^3} \phi(\xi) G(x, \xi, t) d\xi - \int_{\mathbb{R}^3} \phi(\xi) L(x, \xi, t) d\xi \quad (9)$$

where  $\phi$  is an essentially arbitrary function of  $\xi$  and  $G$  and  $L$  are the same as in equation (4) and are made explicit in equation (6). Equation (9) is an equation for the average change of the function  $\phi$  due to collisions. It is obvious that if  $\phi$  is largely arbitrary, then equation (9) implies the Boltzmann equation, equation (4), but this is the step that Maxwell missed.

It is remarkable that, even after the theories of modern physics had been introduced, the Boltzmann equation continued to play a basic role in several areas and not only in the gas theory, where it had become a practical instrument to study the properties of dilute gases.

In 1912 the great mathematician David Hilbert (1862–1943) [17] indicated how to obtain approximate solutions of the Boltzmann equation in the form of a series expansion in powers of a parameter, inversely proportional to the gas density. His paper is also reprinted as Chapter XXII of his treatise entitled *Grundzüge einer allgemeinen Theorie der linearen Integralgleichungen*. The motivation for this circumstance are clearly stated in the preface of the book (“Recently I have added, to conclude, a new chapter on the kinetic theory of gases. [...]. I recognize in the theory of gases the most splendid application of the theorems concerning integral equations”).

Later, about in the same year (1916–1917), Sydney Chapman [18] (1888–1970) and David Enskog [19] (1884–1947) independently obtained approximate solutions of the Boltzmann equation, holding for a dilute gas. Their results were identical for practical purposes, but their methods were widely different both in the spirit and in the details. Enskog introduced a systematic technique which generalized Hilbert's idea whereas Chapman simply extended a method used previously by Maxwell to obtain the values of transport coefficients. Enskog's method was then adopted by S. Chapman and T. G. Cowling in their book *The Mathematical Theory of Non-uniform Gases* and thus became known as the Chapman–Enskog method.

Then for many years no essential progress took place in solving the Boltzmann equation. The ideas of kinetic theory, however, penetrated into other areas, such as radiation transfer, the theory of ionized gases and, subsequently, in the theory of neutron transport. We recall that Lorentz [20] had already considered a particular case of ionized gas, the electrons in a metal; his theory was later extended in order to take into account the holes as well, *i.e.* the carriers of positive charges, and applied to semiconductors as well.

The Boltzmann equation is today the object of a detailed study within a mathematically rigorous theory. This development started, in 1933 with a paper [21] by Tage Gillis Torsten Carleman (1892–1949), who proved a theorem of global existence and uniqueness for a gas of hard spheres in the space-homogeneous case. (*i.e.* he proved that, when the distribution function does not depend on position  $\mathbf{x}$  but only on velocity  $\xi$  and time  $t$ , if we assign the distribution at  $t = 0$ , there is one and only one distribution at subsequent times that coincides with the given distribution at  $t = 0$ ). This theorem was initially proven under the restrictive assumption that the initial data depend on the molecular velocity only through its magnitude. This restriction was removed in a book by the same author, published posthumously and edited by L. Carleson (who completed it in vital points) and O. Frostman [22].

In 1949 Harold Grad (1923–1986) published a paper [13], which became famous because it contained a systematic method to solve the Boltzmann equation by expanding the solution into a series of orthogonal polynomials. As we have hinted at before, however, Grad brought a more fundamental contribution, by introducing in a precise manner the concept of that limit, which is today called Boltzmann-Grad limit.

In the 1950s some significant results were published, such as the exact solutions found independently by C. Truesdell [23] in United States and by V. S. Galkin [24], [25] in Soviet Union, whereas the theory of existence was extended by D. Morgenstern [26], who proved a global existence theorem for a gas of Maxwellian molecules in the space homogeneous case. His work was extended by L. Arkeryd [27], [28] in 1972. The techniques used to obtain the most recent results have become rather complicated, even for a synthetic description.

## 2 Lanford's Theorem

The fundamental question to be settled, *i.e.* whether the *irreversible* Boltzmann equation can be rigorously obtained from *reversible* mechanics was first attacked by O. Lanford in a classical paper [12]. Lanford's paper contains only a sketch of the proof; a more detailed treatment is given in two monographs [11], [29]. The first of these texts presents also an extension [30], [31], due to Illner and Pulvirenti, which gives a global validity result for a gas cloud in all space if the mean free path is large. This is the only global result known so far. In both cases, one can prove propagation of chaos and existence and uniqueness of solutions for the Boltzmann equation.

In order to explain Lanford's Theorem, let  $f^{(s)}(\mathbf{z}^s, t)$  be the  $s$ -particle distribution function introduced in the previous section. Here,  $\mathbf{z}^s = (\mathbf{x}_1, \dots, \mathbf{x}_s, \xi_1, \dots, \xi_s)$  is used as a shorthand for the  $6s$ -dimensional phase point describing the state of the

first  $s$  particles. We write  $\mathbf{z} = (\mathbf{z}^s, \mathbf{z}^{N-s})$ , with the obvious meaning of the symbols. In particular  $f^{(N)}$  is simply denoted by  $f$  and its initial value at time  $t = 0$  by  $f_0$ . We denote by  $T^t$  the operator giving the dynamics of  $N$  hard spheres, *i.e.*  $T^t \mathbf{z}$  denotes the position (in the  $6N$ -dimensional phase space) of the center of a sphere occupying the position  $\mathbf{z}$  at time  $t = 0$ .

We assume that

1. Since the particles are identical,  $f_0(\mathbf{z})$  is symmetric with respect to all particles, *i.e.* for any permutation  $\Pi$  (reordering of the particles)  $f_0(\Pi \mathbf{z}) = f_0(\mathbf{z})$ . Because  $\Pi T^t \mathbf{z} = T^t \Pi \mathbf{z}$ , it follows that also  $f(\cdot, t)$  has this symmetry.

By  $\Omega^s$ ,  $1 \leq s \leq N$ , we denote the phase space of  $s$  particles (phase points leading to multiple collisions, etc., are deleted). The time evolution of the  $s$  particles of which  $f^{(s)}(\mathbf{z}^s, t)$  keeps track is influenced by the interactions of the  $s$  particles with the remaining  $N - s$  particles. In order to be able to quantify these interactions, we need one further assumption on  $f_0$ :

2. We require that  $t \rightarrow f_0(T^t \mathbf{z})$  is continuous for almost all  $\mathbf{z} \in \Omega$ .

Assumption 2 deserves a further comment. If  $\mathbf{z}$  is an  $N$ -particle precollisional phase point and  $\mathbf{z}'$  is the corresponding postcollisional phase point, *i.e.*

$$\mathbf{z} = (\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N, \xi_1, \dots, \xi_i, \dots, \xi_j, \dots, \xi_N)$$

with  $\mathbf{x}_j = \mathbf{x}_i + \mathbf{n}\sigma$  and  $\mathbf{n} \cdot (\xi_i - \xi_j) > 0$ ,

$$\mathbf{z}' = (\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N, \xi_1, \dots, \xi'_i, \dots, \xi'_j, \dots, \xi_N),$$

assumption 2 means that  $f_0$  is continuous outside the contact points and

$$f_0(\mathbf{z}) = f_0(\mathbf{z}'). \quad (10)$$

In other words, “good” initial probability distributions are those which do not distinguish between precollisional and postcollisional configurations.

The evolution equations for the various  $f^{(s)}$  are a simple consequence of the Liouville equation constitute the so-called BBGKY hierarchy:

$$\frac{d}{dt} f^{(s)}(T_\sigma^t \mathbf{z}^s, t) = (Q_{s+1}^\sigma f^{(s+1)})(T_\sigma^t \mathbf{z}^s, t) \quad (11)$$

where we have here added an index  $\sigma$  to the flow operators, as a reminder that these operators do change as  $\sigma \rightarrow 0$ ). Let us analyse what happens to the collision operator in the Boltzmann-Grad limit.

The operator  $Q_{s+1}^\sigma$ , acting on the time evolved marginal distributions via

$$\begin{aligned} Q_{s+1}^\sigma f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_s, \xi_1, \dots, \xi_s, t) \\ = \sum_{j=1}^s (N-s)\sigma^2 \int_{\mathcal{B}} d\mathbf{n} \int d\xi_{s+1} \mathbf{n} \cdot (\xi_j - \xi_{s+1}) \\ f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_s, \mathbf{x}_j - \mathbf{n}\sigma, \xi_1, \dots, \xi_{s+1}, t) \end{aligned} \quad (12)$$

is well defined for all  $t$  and almost all  $\mathbf{z}^s$ . Moreover, we can prove

**Theorem 2.1.** Under the assumptions 1 and 2,  $Q_{s+1}^\sigma f^{(s+1)}(T^t \mathbf{z}^s, t)$  is continuous in  $t$  for almost all  $\mathbf{z}^s$ , and the  $f^s(\cdot, t)$ ,  $1 \leq s \leq N$ , satisfy the BBGKY hierarchy in the mild sense, i.e.

$$\frac{d}{dt}[f^{(s)}(T^t \mathbf{z}^s, t)] = Q_{s+1}^\sigma f^{(s+1)}(T^t \mathbf{z}^s, t) \quad (13)$$

for almost all  $\mathbf{z}^s$ .

We now consider the collision operator and split the integration over  $\mathcal{B}$  into integrations over two hemispheres: On the hemisphere given by  $(\xi_j - \xi_{s+1}) \cdot \mathbf{n} \leq 0$  (incoming configurations), we leave the argument of  $f^{(s+1)}$  untouched, but we make here the change  $\mathbf{n} \rightarrow -\mathbf{n}$  and therefore change this part of the integral to an integral over the hemisphere  $(\xi_j - \xi_{s+1}) \cdot \mathbf{n} \geq 0$ .

On the hemisphere given originally by this latter inequality (outgoing configurations), we leave  $n$  untouched, but we take advantage of the continuity of  $f^{(s+1)}$  through collisions to replace the velocities  $\xi_j$  and  $\xi_{s+1}$  by their precollisional counterparts  $\xi'_j$  and  $\xi'_{s+1}$ . The result of these operations is

$$\begin{aligned} & Q_{s+1}^\sigma f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_s, \xi_1, \dots, \xi_s) \\ &= \sum_{j=1}^s (N-s)\sigma^2 \int d\xi_{s+1} \int_{\mathbf{n} \cdot (\xi_j - \xi_{s+1}) \geq 0} d\mathbf{n} \\ & \quad \mathbf{n} \cdot (\xi_j - \xi_{s+1}) \{ f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_j - \sigma n, \xi_1, \dots, \xi'_j, \dots, \xi'_{s+1}) \\ & \quad \quad - f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_j + \sigma n, \xi_1, \dots, \xi_j, \dots, \xi_{s+1}) \}. \end{aligned} \quad (14)$$

In the Boltzmann-Grad limit,  $N\sigma^2 \rightarrow \alpha$  and formally  $Q^\sigma \rightarrow Q$ , where

$$\begin{aligned} & Q_{s+1} f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_s, \xi_1, \dots, \xi_s) \\ &= \alpha \sum_{j=1}^s \int d\xi_{s+1} \int_{\mathbf{n} \cdot (\xi_j - \xi_{s+1}) \geq 0} d\mathbf{n} \mathbf{n} \cdot (\xi_j - \xi_{s+1}) \\ & \quad \{ f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_j, \xi_1, \dots, \xi'_j, \dots, \xi'_{s+1}) \\ & \quad \quad - f^{(s+1)}(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_j, \xi_1, \dots, \xi_j, \dots, \xi_{s+1}) \}. \end{aligned} \quad (15)$$

As for fixed  $s$ ,  $T_\sigma^t \mathbf{z}^s \rightarrow T_0^t \mathbf{z}^s$  for almost all  $\mathbf{z}^s$  in the limit  $\sigma \rightarrow 0$  ( $T_0^t$  denotes collisionless flow), we expect that the  $f^{(s)}$  will converge to a sequence of functions  $P^{(s)}$  solving the Boltzmann hierarchy:

$$\frac{d}{dt} P^{(s)}(T_0^t \mathbf{z}^s, t) = Q_{s+1} P^{(s+1)}(T_0^t \mathbf{z}^s, t). \quad (16)$$

The relationship of the Boltzmann hierarchy (15) to the Boltzmann equation is the following: If  $P(\cdot, t)$  solves the Boltzmann equation, then

$$P^{(s)}(\mathbf{x}_1, \dots, \mathbf{x}_s, \xi_1, \dots, \xi_s; t) = \prod_{j=1}^s P(\mathbf{x}_j, \xi_j; t)$$

solves the Boltzmann hierarchy. Thus, if the  $P^{(s)}$  in (12) factorize initially and if the factorization is preserved in time (the second *if*, usually referred to as propagation of chaos, must be proved), the Boltzmann hierarchy and the Boltzmann equation are equivalent.

By proving the convergence of  $f^{(s)}$  and propagation of chaos, one completes the objective of validating the Boltzmann equation. First, however, we make some observations which will clarify what we can expect to achieve.

In the derivation of the operator  $Q$ , we chose to represent collision phase points in terms of ingoing configurations. Given the assumed continuity along trajectories, we could as well use the representation in terms of outgoing configurations, and that would lead formally to a limit which is equation (15) with a minus sign in front of the collision operator. Also, if we take the formal limit in the right hand side of equation (12) without first splitting into gain and loss terms, we obtain zero, because the integrations over the two hemispheres compensate each other. We are thus compelled to ask whether the representation in terms of ingoing configurations is the right one, i.e. physically meaningful. A more careful analysis of the validity problem shows that the representation in terms of ingoing configurations follows automatically from hard sphere dynamics and is, indeed, not a matter of an a priori choice.

We consider now equation (12) for  $s = 1$  and discuss the propagation of chaos. Assuming representation in terms of ingoing configurations, the right hand side reads

$$(N - 1)\sigma^2 \int_{\mathbb{R}^3} d\xi_2 \int_{\mathbf{n} \cdot (\xi_1 - \xi_2) \geq 0} d\mathbf{n} \mathbf{n} \cdot (\xi_1 - \xi_2) \{ f^{(2)}(\mathbf{x}_1 + t\xi_1, \mathbf{x}_1 + t\xi_1 - \mathbf{n}\sigma, \xi'_1, \xi'_2; t) - f^{(2)}(\mathbf{x}_1 + t\xi_1, \mathbf{x}_1 + t\xi_1 + \mathbf{n}\sigma, \xi_1, \xi_2; t) \}. \quad (17)$$

In order to get the right hand side of the Boltzmann equation we seem to need the crucial assumption that in the limit  $N \rightarrow \infty$ ,  $\sigma \rightarrow 0$  and  $N\sigma^2 \rightarrow \alpha > 0$  there is a function  $P = P(\mathbf{x}, \xi, t)$  such that

$$\lim_{N \rightarrow \infty} f^{(1)}(\mathbf{x}, \xi, t) = P(\mathbf{x}, \xi, t),$$

$$\lim_{N \rightarrow \infty} f^{(2)}(\mathbf{x}, \mathbf{x} + \mathbf{n}\sigma, \xi_1, \xi_2; t) = P(\mathbf{x}, \xi_1, t)P(\mathbf{x}, \xi_2, t) \quad (18)$$

provided that the configuration is *ingoing*. If this convergence holds, we get the Boltzmann equation in the mild formulation

$$\frac{d}{dt} P(\mathbf{x} + t\xi, \xi, t) = \alpha \int d\xi_* \int_{\mathcal{B}} d\mathbf{n} \mathbf{n} \cdot (\xi - \xi_*) (P' P'_* - P P_*) (\mathbf{x} + t\xi, \xi, t).$$

Our convention here is that  $P_*(\mathbf{x} + t\xi, \xi, t) = P(\mathbf{x} + t\xi, \xi_*, t)$ , etc.

It turns out that (18) is a statement stronger than what we need. Worse, (18) can be violated even at time  $t = 0$  for quite reasonable  $f^{(2)}$ 's, as can be shown by examples. The form of propagation of chaos which we will be able to prove is that

$$f^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \xi_1, \xi_2; t) \rightarrow P(\mathbf{x}_1, \xi_1, t)P(\mathbf{x}_2, \xi_2, t)$$

for almost all  $\mathbf{x}_1, \mathbf{x}_2, \xi_1, \xi_2$  (and not on a manifold of codimension one, as in (18)).

In [11] an example of a discrete velocity model is discussed for which the derivation done in the present section fails completely. Given that convergence of the derivatives is not to be expected, what we are going to do is to look at the solution of the BBGKY hierarchy and the Boltzmann hierarchy as a whole (and not at their derivatives) and show that the first converge a.e. to the second. The solution concept which allows us to do this is a series solution concept which we now introduce.

After integration from 0 to  $t$ , we get from (11) that

$$f^{(s)}(T_\sigma^t \mathbf{z}^s, t) = f_0^{(s)}(\mathbf{z}^s) + \int_0^t dt_1 (Q_{s+1}^\sigma f^{(s+1)})(T_\sigma^{t_1} \mathbf{z}^s, t_1)$$

or

$$f^{(s)}(\mathbf{z}^s, t) = (S_\sigma(t) f_0^{(s)})(\mathbf{z}^s) + \int_0^t dt_1 S_\sigma(t - t_1) Q_{s+1}^\sigma f^{(s+1)}(\mathbf{z}^s, t_1)$$

where  $S_\sigma(t) P(\mathbf{z}^s) = P(T_\sigma^{-t} \mathbf{z}^s)$ .

By iterating the last equation  $N - s$  times and using the convention that  $f_0^{(s)} = 0$  for  $s > N$ , we can express  $f^{(s)}(\mathbf{z}^s, t)$  as a finite sum of multiple integrals involving only the functions  $f_0^{(r)}$  for  $r \geq s$ :

$$\begin{aligned} f^{(s)}(\mathbf{z}^s, t) &= \sum_{n=0}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2, \dots \\ &\quad \dots, \int_0^{t_{n-1}} dt_n S_\sigma(t - t_1) Q_{s+1}^\sigma S_\sigma(t_1 - t_2), \dots, Q_{s+n}^\sigma S_\sigma(t_n) f_0^{(s+1)}(\mathbf{z}^s) \end{aligned} \tag{19}$$

Note that the sum is actually finite because of our convention. For  $s = N$ , (19) reduces to  $f^{(N)}(\mathbf{z}, t) = S_\sigma(t) f_0^{(N)}(\mathbf{z})$ , which is just the solution of the so-called Liouville equation, an exact partial differential equation which rules the time evolution of  $f^{(N)}(\mathbf{z}, t)$ .

Equation (19) is an equality which holds for almost all  $\mathbf{z}^s$ . Similarly, a formal series solution can be written down for the Boltzmann hierarchy (16). It is

$$\begin{aligned} P^{(s)}(\cdot, t) &= \sum_{n=0}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2, \dots \\ &\quad \dots, \int_0^{t_{n-1}} dt_n S_0(t - t_1) Q_{s+1} S_0(t_1 - t_2), \dots, Q_{s+n} S_0(t_n) P_0^{(s+n)} \end{aligned} \tag{20}$$

where

$$S_0(t) P(\mathbf{z}^s) = P(T_0^{-t} \mathbf{z}^s).$$

In contrast to (19), (20) is an infinite series, and the question of convergence becomes critical.

There is an obvious trace problem in the definition of  $Q$  on  $L^1$ -functions; the series solution concept which we adopt nicely avoids this problem, because each term of the series (20) involves  $P_0^{(s)}$  evaluated at phase points which are computed by repeatedly

adjoining collision partners (this is what  $Q$  does) and backward free streaming (this is what  $S_0$  does), such that each term in the right hand side of (20) makes sense if  $P_0^{(s)}$  is assumed to be sufficiently smooth.

We emphasize at this point that (19) and (20) are profoundly different, in spite of their formal similarity. From a physical point of view, (19) describes a Hamiltonian (reversible) dynamical system, while (20) describes a dissipative evolution which is compatible with the  $H$ -theorem. Also, technically speaking,  $Q$  is more singular than  $Q^\sigma$ : Indeed,  $Q_{s+1}$  involves the trace of  $P^{(s+1)}$  on a manifold of codimension three, while  $Q_{s+1}^\sigma$  needs the trace of  $f^{(s+1)}$  on a manifold of codimension one (the sphere shrinks to a point in the limit).

On the other hand, the presence of the flow  $T_\sigma^t$  in (19) makes it hard to interpret the BBGKY hierarchy from a pure PDE point of view. The hierarchy in equation (11) is a family of equations which can only be established once the flow  $T_\sigma^t$  is defined and once the properties of this flow are well understood.

We are now able to formulate our rigorous validity result. Consider a system of  $N$  particles in a region  $\Omega$ . We shall assume either  $\Omega = \mathbb{R}^3$  or  $\Omega \subset \mathbb{R}^3$  bounded, with a smooth boundary.  $T_\sigma^t$  and  $T_0^t$  will refer to the  $N$ -particle dynamics and the free flow, both with reflecting boundary conditions on  $\partial\Omega$ . The case in which  $\Omega$  is a rectangle with periodic boundary conditions can be considered as well.

Suppose that  $P_0^{(s)}(\mathbf{z}^s) = \prod_{i=1}^s P_0(\mathbf{x}_i, \xi_i)$  is the factorizing initial value for the  $s$ -th equation in the Boltzmann hierarchy (molecular chaos or statistical independence is taken for granted at  $t = 0$ ), and that  $f_0^{(s)}(\mathbf{z}^s)$  is the initial value for the  $s$ -th equation in the BBGKY hierarchy. We send  $N \rightarrow \infty$ ,  $\sigma \rightarrow 0$  in such a way that  $N\sigma^2 = \alpha$  and assume that

- i) if  $(\Omega \times \mathbb{R}^3)^{s,\sigma}_{\neq} = \{\mathbf{z}^s \in \Omega^s \times \mathbb{R}^3; |\mathbf{x}_i - \mathbf{x}_j| > \sigma, i \neq j, \sigma \geq 0\}$ , then the  $f_0^{(s)}$  are continuous on  $(\Omega \times \mathbb{R}^3)^{s,\sigma}_{\neq}$  and at the collision points (continuity along trajectories).  $P_0$  is continuous and  $\lim_{N \rightarrow \infty} f_0^{(s)} = P_0^{(s)}$  uniformly on compact subsets of  $(\Omega \times \mathbb{R}^3)^{s,\sigma}_{\neq}$  for all  $s = 1, 2, \dots$
- ii) there are positive constants  $\beta$ ,  $C$  and  $b$  such that

$$\sup_{\mathbf{z}^s} f_0^{(s)}(\mathbf{z}^s) \exp \left\{ \beta \sum_{i=1}^s |\xi_i|^2 \right\} \leq C \cdot b^s \quad \text{for all } s. \quad (21)$$

Finally we can state Lanford's theorem:

**Theorem 2.2.** *Suppose that i) and ii) hold. Then, on a sufficiently small interval  $[0, t_0]$ , the series solution  $f^{(s)}(\cdot, t)$  of the BBGKY hierarchy converges in the Boltzmann-Grad limit almost everywhere to the series solution of the Boltzmann hierarchy  $P^{(s)}(\cdot, t)$ . This solution exists, is unique and is of the form*

$$P^{(s)}(\mathbf{z}^s, t) = \prod_{i=1}^s P(\mathbf{x}_i, \xi_i, t),$$

where  $f$  is a mild solution of the Boltzmann equation to the initial value  $f_0$ .

For the proof of this and other results in this section, we refer to a previously quoted monograph [11].

Lanford's method gives a local result for rather general initial values. However, for suitably small initial data one can prove global validity by replacing the smallness condition on time by a largeness condition on the mean free path; consider, for example, hard sphere dynamics in all of  $\mathbb{R}^3$  and initial data which decay sufficiently fast at infinity, a situation which we address in this section.

First, we note that certain steps of the proof discussed in the previous section are completely general; therefore, a global result will be proved if we can control the series solution for the BBGKY and Boltzmann hierarchies globally.

As before, we assume a factorizing initial value

$$P_0^{(s)}(\mathbf{z}^s) = \prod_{i=1}^s P_0(\mathbf{x}_i, \xi_i)$$

and the Boltzmann-Grad limit  $N \rightarrow \infty, \sigma \rightarrow 0, N\sigma^2 = \alpha$ .

In addition, suppose that

i) the  $f_\sigma^{(s)}(\cdot, 0)$  are continuous on  $(\mathbb{R}^3 \times \mathbb{R}^3)^{s,\sigma}_{\neq}$  and

$$\lim_{N \rightarrow \infty} f_\sigma^{(s)}(\cdot, 0) = P_0^{(s)}$$

uniformly on compact subsets of  $(\mathbb{R}^3 \times \mathbb{R}^3)^{s,0}_{\neq}$ .

ii) there are constants  $\beta_0 > 0, c > 0$  and  $b > 0$  such that

$$\sup_{\mathbf{z}^s} \left( f_\sigma^{(s)}(\mathbf{z}^s, 0) \exp \left( \beta_0 \sum_{i=1}^s (|\xi_i|^2 + |\mathbf{x}_i|^2) \right) \right) \leq cb^s.$$

Under these hypotheses, we have [30], [31]:

**Theorem 2.3.** *Suppose that i) and ii) hold. Then, if  $b\alpha$  is sufficiently small, the series solution  $f_\sigma(\cdot, t)$  of the BBGKY hierarchy converges for all  $t > 0$  in the Boltzmann-Grad limit almost everywhere to the series solution  $P(\cdot, t)$  of the Boltzmann hierarchy. The latter factorizes as*

$$P^{(s)}(\mathbf{z}^s, t) = \prod_{i=1}^s P(\mathbf{x}_i, \xi_i, t)$$

and  $P$  is a mild global solution of the Boltzmann equation for the initial value  $P_0$ . Moreover,  $f_\sigma^{(s)}$  and  $P^{(s)}$  satisfy the estimates

$$0 \leq f_\sigma^{(s)}(\mathbf{z}^s, t) \leq (cb)^s \exp(-\beta_0 \cdot I(T^{-t} \mathbf{z}^s))$$

(where  $I(\mathbf{z}^s) = \sum_{i=1}^s \mathbf{x}_i^2$ ),

$$0 \leq P(\mathbf{x}, \xi, t) \leq (c \cdot b) \exp(-\beta_0 (\mathbf{x} - t \xi)^2).$$

The constant  $c$  is independent of  $N$  and  $s$ .

For the proof we refer again to the previously quoted monograph [11].

### 3 Existence and uniqueness results

The well-posedness of the initial value problem (IVP in the sequel) for the Boltzmann equation means that we prove that there is a unique nonnegative solution preserving the energy and satisfying the  $H$ -theorem, from a positive initial datum with finite energy and entropy. However, for general initial data, it is difficult, and until now not known, whether such a well-behaved solution can be constructed globally in time. The difficulty in doing this is obviously related to the nonlinearity of the collision operator and the apparent lack of conservation laws or a priori estimates preventing the solution from becoming singular in finite time.

A complete validity discussion for the Boltzmann equation will automatically contain existence and uniqueness results. Consequently, by the discussion of the previous section, we already have some existence and uniqueness theorems. Unfortunately, a validity proof involves several hard additional steps beyond existence and uniqueness, like estimates for the BBGKY hierarchy. Therefore, the Boltzmann equation has been validated rigorously only in the few simple situations which we discussed in the previous section (locally in time, and globally for a rare gas cloud in all space).

Existence (and in some situations uniqueness) of solutions to IVP is known for a much larger variety of cases, and it is our purpose now to survey these results.

When the distribution function of a gas is not depending on the space variable, the equation is considerably simplified. The collision operator is basically Lipschitz continuous in  $L^1_+$  and the equation becomes globally solvable in time. Moreover, uniqueness, asymptotic behavior and a theory of classical solutions have been established. The theory for the spatially homogeneous Boltzmann equation begins in the early thirties and can be considered rather complete; unfortunately the homogeneous case is hardly of interest for applications. The reader interested in this theory should consult [11].

If the solution is initially sufficiently close to a Maxwellian, it is possible to prove that a solution can be constructed globally in time, and we have uniqueness and asymptotic behavior. The approach is based on the analysis of the linearized Boltzmann operator, which leads us to a differential inequality of the type

$$\frac{d}{dt}y \leq -ky + y^2$$

where  $y = y(t)$  is some norm of the deviation of the solution from the Maxwellian and  $k$  is a positive number. Therefore, if  $y(0)$  is sufficiently small, we can control the solution for all times. As we said, the basic ingredient is good control of the linearized Boltzmann operator. This theory is discussed in [11].

If the initial value is close to a homogeneous distribution, a solution starting from it can be constructed globally in time. Uniqueness and asymptotic behavior can also be proved. The main idea is explained in [11].

Except the first one, all these results have a perturbation character. The knowledge of particular solutions helps to construct other solutions which are close to the original ones. The general IVP is poorly understood, although a significant and somewhat unexpected step was performed in the late eighties [32]. Consider an equation similar

to the Boltzmann equation for which we have conservation of mass and energy and the  $H$ -theorem. Denote by  $f^\epsilon(t)$  the solutions. Here,  $\epsilon$  is a regularization parameter such that the solutions formally converge to a solution of the Boltzmann equation in the limit  $\epsilon \rightarrow 0$ . The conservation laws yield the existence of a weak limit denoted by  $f(t)$ . However, since the collision operator is quadratic in  $f$ , it cannot be weakly continuous. Thus it does not follow by general arguments that  $f(t)$  solves the Boltzmann equation. Nevertheless, some smoothness gained by the streaming operator gives enough compactness to prove that  $f(t)$  actually solves the Boltzmann equation in the mild sense.

The method gives neither uniqueness nor energy conservation, but the entropy is seen to decrease along the solution trajectories.

Let us begin with some notation and a rather standard definition. Let  $\Lambda f$  denote the left-hand side of the Boltzmann equation and

$$f^\#(x, \xi, t) = f(x + \xi t, \xi, t).$$

**Definition 3.1.** A measurable function  $f = f(x, \xi, t)$  on  $[0, \infty) \times \mathbb{R}^3 \times \mathbb{R}^3$  is a mild solution of the Boltzmann equation for the (measurable) initial value  $f_0(x, \xi)$  if for almost all  $(x, \xi)$   $Q_\pm(f, f)^\#(x, \xi, \cdot)$  are in  $L^1_{\text{loc}}[0, \infty)$ , and if for each  $t \geq 0$

$$f^\#(x, \xi, t) = f_0(x, \xi) + \int_0^t Q(f, f)^\#(x, \xi, s) ds.$$

One of the key ideas used by DiPerna and Lions [32] to prove a general existence theorem was to relax the solution concept even further, such that the bounds provided by the energy conservation and the  $H$ -theorem could be put to the best use, and then to regain mild solutions via a limit procedure. They called the relaxed solution concept “renormalized solution” and defined it in the following way:

**Definition 3.2.** A function  $f = f(x, \xi, t) \in L^1_+(\mathbb{R}_+^+ \times \mathbb{R}^3 \times \mathbb{R}^3)$  is called a renormalized solution of the Boltzmann equation if

$$Q_\pm(f, f) + f \in L^1_{\text{loc}}(\mathbb{R}_+ \times \mathbb{R}^3 \times \mathbb{R}^3) \quad (22)$$

and if for every Lipschitz continuous function  $\beta: \mathbb{R}_+ \rightarrow \mathbb{R}$  which satisfies  $|\beta'(t)| \leq C/(1+t)$  for all  $t \geq 0$  one has

$$\Lambda \beta(f) = \beta'(f) Q(f, f)$$

in the sense of distributions.

DiPerna and Lions [32] noticed that renormalization would actually give mild solutions, according to the following

**Lemma 3.1.** *Let  $f \in (L^1_{\text{loc}} \times \mathbb{R}^3 \times \mathbb{R}^3)$ . If  $f$  satisfies (22) and (23) with  $\beta(t) = \ln(1+t)$ , then  $f$  is a mild solution of the Boltzmann equation. If  $f$  is a mild solution of the Boltzmann equation and if  $Q_\pm(f, f)/(1+f) \in L^1_{\text{loc}}(\mathbb{R}_+ \times \mathbb{R}^3 \times \mathbb{R}^3)$ , then  $f$  is a renormalized solution.*

Their main result is:

**Theorem 3.1** (DiPerna and Lions [32]). *Suppose that  $f_0 \in L^1_+(\mathbb{R}^3 \times \mathbb{R}^3)$  is such that*

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} f_0(1 + |\mathbf{x}|^2 + |\xi|^2) d\mathbf{x} d\xi < \infty$$

and

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} f_0 |\ln f_0| d\mathbf{x} d\xi < \infty.$$

*Then there is a renormalized solution such that  $f \in C(\mathbb{R}_+, L^1(\mathbb{R}^3, \mathbb{R}^3))$ ,  $f|_{t=0} = f^0$ .*

## 4 Concluding remarks

The existence theorem of DiPerna and Lions is rightly considered as a basic result of the mathematical theory of the Boltzmann equation. Unfortunately, it is far from providing a complete theory, since there is no proof of uniqueness; in addition, there is no proof that energy is conserved and conservation of momentum can be proved only globally and not locally. More complete results concerning conservation equations are only known in the case of solutions depending on just one space coordinate [33].

Fortunately, a more complete theory is available for slow flows, which have gained a renewed interest in recent applications. In this case, one can exploit the fact that the distribution function is close to a space homogeneous Maxwellian to take advantage of rigorous perturbation methods to establish a global existence and uniqueness theory.

Before concluding, it seems appropriate to deal briefly with the fact that the Boltzmann equation is not only a conceptual but also a practical tool. When an aerospace engineer studies the re-entry of a space shuttle, he must take into account the fact that the description of air as a continuum, usually adopted in the design of airplanes, no longer holds in the upper part of atmosphere and he must use the Boltzmann equation. If we want to study the motion of the minutest particles which pollute our atmosphere, we must again, because of the reduced size of these particles, abandon the model of air as a continuum and use the Boltzmann equation.

Engineers use suitable modifications of the same equation to study important phenomena in other fields of modern technology, from the motion of neutrons in fission nuclear reactors to that of charged particles in the sought for fusion reactors, from the radiation in a combustion chamber to the motion of charge carriers in the very small semiconductor *chips* for computers.

A third area of application of rarefied gas dynamics has emerged in the last few years and has been hinted at above. Small size machines, called micromachines, are being designed and built. Their typical sizes range from a few microns to a few millimeters. Slow rarefied flow phenomena that are more or less laboratory curiosities in machines of more usual size can form the basis of important systems in the micromechanical domain [34]. In fact, rarefied gas flows occur in many micro-electro-mechanical systems (MEMS), such as actuators, microturbines, gas chromatographs, and micro air vehicles

(MAVs). A correct prediction of these flows is important to design and develop MEMS. Nanoscale design occurs for computer components as well and is no longer limited to chip technology but extends to mechanical devices as well. In a modern disk drive, the read/write head floats at distances of the order of 50 nm above the surface of the spinning platter. The prediction of the vertical force on the head (as obtained from the pressure distribution in the gas) is a crucial design calculation since the head will not accurately read or write if it flies too high. If the head flies too low, it can catastrophically collide against the platter. Micro-channels may have further computer applications because they are supposed to dissipate the heat generated in microchips more effectively than fans, and may be used as a more practical cooling system in integrated circuit chips.

Boltzmann would have been pleased by these technological applications. He was deeply interested in technology (in particular, he predicted the superiority of the airplane with respect to the dirigible) and praised more than once the role of technology in the development of science, as one can see from the following two quotations (for more details, see [35]):

“However much science prides itself on the ideal character of its goal, looking down somewhat contemptuously on technology and practice, it cannot be denied that it took its rise from a striving for satisfaction of purely practical needs. Besides, the victorious campaign of contemporary natural science would never have been so incomparably brilliant, had not science found in technologists such capable pioneers.” (October 1902).

“That is why I do not regard technological achievements as unimportant by-products of natural science but as logical proofs. Had we not attained these practical achievements, we should not know how to infer. Only those inferences are correct that lead to practical success.” (January 1905).

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*Über die Unentbehrlichkeit der Atomistik in den Naturwissenschaften*

Drawing by Karl Przibram

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# ***H*-theorem and beyond: Boltzmann's entropy in today's mathematics**

Cédric Villani

## **Introduction**

In spite of his proudly unpolished writing and his distrust for some basic mathematical concepts (such as infinity or continuum), Ludwig Boltzmann has made major contributions to mathematics. In particular, the notion of *entropy*, and the famous *H*-theorem, have been tremendous sources of inspiration to (a) understand our (physical) world in mathematical terms; (b) attack many (purely) mathematical problems. My purpose in this lecture is to develop and illustrate these claims. Before going on, I shall provide some quotations about the influence of Boltzmann on the science of his time. There is no need to recall how much Einstein, for instance, praised Boltzmann's work in statistical mechanics. But to better illustrate my point, I will quote some great *mathematicians* talking about Boltzmann:

*All of us younger mathematicians stood by Boltzmann's side.*

Arnold Sommerfeld (about a debate taking place in 1895)

*Boltzmann's work on the principles of mechanics suggests the problem of developing mathematically the limiting processes (...) which lead from the atomistic view to the laws of motion of continua.*

David Hilbert (1900)

*Boltzmann summarized most (but not all) of his work in a two volume treatise Vorlesungen über Gastheorie. This is one of the greatest books in the history of exact sciences and the reader is strongly advised to consult it.*

Mark Kac (1959)

This lecture is an extended version of a conference which I gave at various places (Vienna, Münich, Leipzig, Brisbane, Pisa) on the occasion of the hundredth anniversary of the death of Boltzmann. It is a pleasure to thank the organizers of these events for their excellent work, in particular Jakob Yngvason, Herbert Spohn, Manfred Salmhofer, Bevan Thompson, and Luigi Ambrosio. Thanks are also due to Wolfgang Wagner for his comments. The style will be somewhat informal and I will often cheat for the sake of pedagogy; more precise information and rigorous statements can be retrieved from the bibliography.

## 1 1872: Boltzmann's *H*-theorem

The so-called Boltzmann equation models the dynamics of rarefied gases via a time-dependent density  $f(x, v)$  of particles in phase space ( $x$  stands for position,  $v$  for velocity):

$$\frac{\partial f}{\partial t} + v \cdot \nabla_x f = Q(f, f).$$

Here  $v \cdot \nabla_x$  is the transport operator, while  $Q$  is the bilinear collision operator:

$$Q(f, f) = \int_{\mathbb{R}_{v_*}^3 \times S^2} B [f(v')f(v'_*) - f(v)f(v_*)] dv_* d\sigma;$$

and  $B = B(v - v_*, \sigma) \geq 0$  is the collision kernel. The notation  $v'$ ,  $v'_*$  denotes pre-collisional velocities, while  $v$ ,  $v_*$  stand for post-collisional velocities (or the reverse, it does not matter in this case). I refer to my review text in the *Handbook of Mathematical Fluid Dynamics* [19] for a precise discussion, and a survey of the mathematical theory of this equation.

According to this model, under ad hoc boundary conditions, ***the entropy  $S$  is non-decreasing*** in time. That is, if one defines

$$S(f) = -H(f) := - \int_{\Omega \times \mathbb{R}_v^3} f(x, v) \log f(x, v) dv dx,$$

then the time-derivative of  $S$  is always nonnegative.

Boltzmann's theorem is more precise than just that: It states that a (strictly) positive amount of entropy is produced at time  $t$ , unless the density  $f$  is ***locally Maxwellian*** (hydrodynamic): that is, unless there exist fields  $\rho$  (scalar),  $u$  (vector) and  $T$  (scalar) such that

$$f(x, v) = M_{\rho, u, T}(v) = \frac{\rho(x) e^{-\frac{|v-u(x)|^2}{2T(x)}}}{(2\pi T(x))^{3/2}}.$$

In words, a hydrodynamic state is a density whose velocity dependence is Gaussian, with scalar covariance – at each position  $x$ . It depends on three local parameters: density  $\rho$ , velocity  $u$ , and temperature  $T$  (temperature measures the variance of the velocity distribution).

The time-derivative of the entropy is given by an explicit formula:

$$\frac{dS}{dt} = -\frac{dH}{dt} = \int_{\Omega} D(f(t, x, \cdot)) dx,$$

where

$$D(f) = \frac{1}{4} \int_{v, v_*, \sigma} B [f(v')f(v'_*) - f(v)f(v_*)] \log \frac{f(v')f(v'_*)}{f(v)f(v_*)} dv dv_* d\sigma \geq 0.$$

So Boltzmann's theorem can be recast as

$$[D(f) = 0] \iff [f(v) = M_{\rho u T}(v) \text{ for some parameters } \rho, u, T].$$

Let me now make a *disclaimer*. Although Boltzmann's *H*-theorem is 135 years old, present-day mathematics is unable to prove it rigorously and in satisfactory generality. The obstacle is the same as for many of the famous basic equations of mathematical physics: we don't know whether solutions of the Boltzmann equations are smooth enough, except in certain particular cases (close-to-equilibrium theory, spatially homogeneous theory, close-to-vacuum theory). For the moment we have to live with this shortcoming.

## 2 Why is the *H*-theorem beautiful?

Some obvious answers are:

- (i) Starting from a model based on reversible mechanics and statistics, Boltzmann finds irreversibility (which triggered endless debates).
- (ii) This is an exemplification of the Second Law of Thermodynamics (entropy can only increase in an isolated system), but it is a *theorem* – as opposed to a postulate.

Here are some more “mathematical” reasons:

- (iii) Its proof is clever and beautiful, although not perfectly rigorous.
- (iv) It provides a powerful a priori estimate on a complicated nonlinear equation.
- (v) The *H*-function has a statistical (microscopic) meaning: it says how exceptional the distribution function is.
- (vi) The *H*-theorem gives some qualitative information about the evolution of the (macroscopic) distribution function.

All these ideas are still crucial in current mathematics, as I shall discuss in the sequel.

## 3 The *H*-theorem as an a priori estimate on a complicated nonlinear equation

Let  $f(t, \cdot)$  be a solution of the full Boltzmann equation. The *H*-theorem implies the estimate

$$H(f(t)) + \int_0^t \int D(f(s, x, \cdot)) dx ds \leq H(f(0)), \quad (1)$$

where *H* stands for the *H*-function, and *D* for the associated dissipation functional. There is in fact equality in (1) if the solution is well-behaved, but in practise it is easier to prove the inequality, and this is still sufficient for many purposes.

Inequality (1) is in fact *two* a priori estimates! Both the finiteness of the entropy and the finiteness of the (integrated) production of entropy are of great interest.

As a start, let us note that the finiteness of the entropy is a weak and general way to prevent *concentration* (“clustering”). For instance, the bound on *H* guarantees that the solution of the Boltzmann equation never develops Dirac masses. This fact is physically obvious, but not so trivial from the mathematical point of view.

The first important use of the entropy as an a priori estimate goes back to Arkeryd [2] in his study of the spatially homogeneous Boltzmann equation – exactly hundred years after Boltzmann’s discovery!

Both the entropy estimate and the entropy production estimate are crucial in the famous 1989 DiPerna–Lions stability theorem [10]. To simplify things, this theorem states that *Entropy, entropy production and energy bounds guarantee that a limit of solutions of the Boltzmann equation is still a solution of the Boltzmann equation.*

It is not just for the sake of elegance that DiPerna and Lions used these bounds: save for estimates which derive from conservation laws, entropy bounds are still the *only* general estimates known to this day for the full Boltzmann equation!

Robust and physically significant, entropy and entropy production bounds have been used systematically in partial differential equations and probability theory, for hundreds of models and problems. Still today, this is one of the first estimates which one investigates when encountering a new model.

Let me illustrate this with a slightly unorthodox use of the entropy production estimate, on which I worked together with Alexandre, Desvillettes and Wennberg [1]. The regularizing properties of the evolution under the Boltzmann equation depend crucially on the microscopic properties of the interaction: long-range interactions are usually associated with regularization. At the level of the Boltzmann collision kernel, long range results in a divergence for small collision angles. As a typical example, consider a collision kernel  $B = |v - v_*|^\gamma b(\cos \theta)$ , where

$$b(\cos \theta) \sin \theta \simeq \theta^{-(1+\nu)}, \quad 0 < \nu < 2$$

as  $\theta \rightarrow 0$ . (This corresponds typically to a radially symmetric force like  $r^{-s}$  in dimension 3, and then  $\nu = 2/(s-1)$ .)

The regularizing effect of this singularity can be seen on the entropy production. Indeed, we could prove an estimate of the form

$$\left\| (-\Delta_v)^{\nu/4} \sqrt{f} \right\|_{L^2_{loc}}^2 \leq C \left( \int f \, dv, \int f |v|^2 \, dv, H(f) \right) \left[ D(f) + \int f (1+|v|^2) \, dv \right].$$

Thus, some regularity is controlled by the entropy production, together with natural physical estimates (mass, energy, entropy).

## 4 The statistical meaning of the $H$ -function

As I said before, the basic statistical information contained in the  $H$ -function is about how exceptional the distribution function is. This interpretation is famous but still retains some of its mystery today. It appears not only in Boltzmann’s work, but also in Shannon’s theory of information, which in some sense announced the ocean of information in which we are currently living.

For those who believe that entropy has always been a crystal-clear concept, let me recall a famous quote by Shannon: “*I thought of calling it “information”. But the word was overly used, so I decided to call it “uncertainty”. When I discussed it with John*

*von Neumann, he had a better idea: (...) “You should call it entropy, for two reasons. In first place your uncertainty has been used in statistical mechanics under that name, so it already has a name. In second place, and more important, no one knows what entropy really is, so in a debate you will always have the advantage.”* (Note the influence of mathematicians again, for good or for bad...)

Let me recall some basic concepts from information theory; for more information (if I may say) on the subject the reader can consult the classical treatise by Shannon [16], and the more recent one by Cover and Thomas [7].

In a nutshell, the Shannon–Boltzmann entropy  $S = -H = -\int f \log f$  quantifies (in logarithmic scale) how much information there is in a “random” signal, or a language; think of  $f$  as the density of the distribution of the signal. For instance, a deterministic language means complete predictability, so no surprise and no information (think of a public statement by a politician); thus  $S = -\infty$ .

When there is a nontrivial reference probability measure, the proper formula for  $H$  is

$$H_\mu(v) = \int \rho \log \rho d\mu; \quad v = \rho \mu.$$

Let me mention in passing another hero of modern information theory: the **Fisher information**  $\int \frac{|\nabla f|^2}{f}$  quantifies how difficult it is to reconstruct the mean value of  $f$  from the observations. Also it plays an important role in many problems of “pure” mathematics; see for instance Voiculescu [24]. But this is a different story, so I won’t develop on this fascinating subject.

From a physical point of view, the entropy functional measures the **volume** of **microstates** associated, to some degree of accuracy in macroscopic observables, to a given **macroscopic** configuration, or observable distribution function. All words are meaningful here, in particular the concept of entropy implies an observation, with some margin of error. (*Entropy* is an *anthropic* notion, as the joke goes.) The basic question related to entropy is “How exceptional is the observed configuration?”

To make this fuzzy discussion a bit more concrete, I shall recall a classical computation by Boltzmann. Take  $N$  identical particles, to be distributed over  $k$  boxes, and let  $f_1, \dots, f_k$  be some (rational) frequencies (i.e. numbers in  $[0, 1]$  adding up to 1). Let  $N_j$  be the number of particles in the box number  $j$ . Let further  $\Omega_N(f)$  be the number of configurations such that  $N_j/N = f_j$  for any  $j$ . ( $\Omega_N(f)$  might be zero, so I shall implicitly assume that  $N$  is so chosen that this is not the case.)

After a little bit of combinatorics (which classically rely on Stirling’s formula, but the latter can be dispensed with [7]), one finds

$$\#\Omega_N(f_1, \dots, f_k) \sim e^{-N \sum f_j \log f_j} \quad \text{as } N \rightarrow \infty,$$

in the sense that  $(1/N) \log \#\Omega_N$  converges to  $-\sum f_j \log f_j$ , which is nothing but the discrete version of  $-\int f \log f$ .

The famous **Sanov theorem**, part of the theory of large deviations [8], generalizes this computation, and puts the intuition of Boltzmann on rigorous mathematical

grounds. Let  $x_1, \dots, x_n, \dots$  be independent “microscopic variables” with law  $\mu$ ; define

$$\hat{\mu}^N := \frac{1}{N} \sum_{i=1}^N \delta_{x_i}.$$

This is a random measure, usually called the empirical measure. It contains all the information which is “macroscopically observable” if we cannot distinguish between different particles.

How will the values of  $\hat{\mu}^N$  be distributed for large  $N$ ? The fuzzy answer is that  $\hat{\mu}^N$  visits measures more or less often according to their entropy. Formally:

$$\mathbb{P}[\hat{\mu}^N \simeq \nu] \sim e^{-NH_\mu(\nu)} d(\nu)$$

A rigorous writing of Sanov’s theorem involves three limiting processes, and there is no way one can do without them. Let  $(\varphi_k)_{k \in \mathbb{N}}$  be a dense sequence of Lipschitz functions (think of them as “observables”); let  $\nu$  be a measure (think of it as the “guessed empirical measure”); and let  $\varepsilon > 0$  be some real number (think of it as an “observation error” measured on some choice of observables). Define

$$\Omega(N, \varepsilon, k) := \left\{ (x_1, \dots, x_N); \left| \frac{\varphi_j(x_1) + \dots + \varphi_j(x_N)}{N} - \int \varphi_j \, d\nu \right| < \varepsilon \text{ for all } j \leq k, \right\}$$

(This is the set of data compatible with the observations, given the admissible error.) Then

$$H_\mu(\nu) = \lim_{k \rightarrow \infty} \limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} \left( -\frac{1}{N} \log \mathbb{P}_{\mu^{\otimes N}}[\Omega(N, \varepsilon, k)] \right).$$

Behind the technical trickery, the reader should recognize the famous formula written on Boltzmann’s grave,  $S = k \log W$ .

## 5 Boltzmann’s ideas revisited by Voiculescu

In the past decade, Voiculescu made spectacular contributions to operator theory by adapting some ideas coming from statistical mechanics and statistics. [24] A few reminders about the theory of von Neumann algebras will convince the nonexpert reader that this has apparently nothing to do with the questions upon which Boltzmann has worked.

Initially motivated by quantum mechanics and group representation theory, the study of von Neumann algebras has evolved into a mathematical domain on its own, with many respectable internal problems. Let  $H$  be a separable Hilbert space, and let  $\mathcal{B}(H)$  stand for the space of bounded operators on  $H$ , equipped with the operator norm. By definition, a von Neumann algebra  $\mathcal{A}$  is a sub-algebra of  $\mathcal{B}(H)$  which (a) contains the identity operator  $I$ ; (b) is stable by passage to the adjoint,  $A \rightarrow A^*$ ; (c) is closed for the weak topology, defined by the linear forms  $A \rightarrow \langle A\xi, \eta \rangle$  (for any two vectors  $\xi, \eta$  in  $H$ ).

The classification of von Neumann algebras is still an active topic with famous unsolved basic questions. By definition, a *type II<sub>1</sub> factor* is an infinite-dimensional von Neumann algebra  $\mathcal{A}$  with trivial center, equipped with a *tracial state*, i.e. a linear form  $\tau: \mathcal{A} \rightarrow \mathbb{C}$  such that (a)  $\tau(A^*A) \geq 0$  for any  $A \in \mathcal{A}$  (positivity property); (b)  $\tau(I) = 1$  (unit mass property); (c)  $\tau(AB) = \tau(BA)$  (traciality). Then  $(\mathcal{A}, \tau)$  is called a *noncommutative probability space*.

The analogy between “classical” and noncommutative probability spaces can be pursued to some extent. In particular, one can define the *noncommutative distribution function* of an  $n$ -tuple  $(A_1, \dots, A_n)$  of self-adjoint elements in  $(\mathcal{A}, \tau)$ : this is just the collection of all traces of all (noncommutative) polynomials of  $A_1, \dots, A_n$ . (So this is a bunch of complex numbers, say  $\tau(A_1), \tau(A_1 A_2), \tau(A_1^2 A_3 A_2)$ , etc.)

Some of these noncommutative probability spaces can be realized as “macroscopic” limits of large random matrices. Let indeed  $X_1^{(N)}, \dots, X_n^{(N)}$  be an  $n$ -tuple of random  $N \times N$  matrices. If the trace of any noncommutative polynomial constructed with these matrices has a definite limit, then one may obtain (via some nonessential abstract construction) elements  $A_1, \dots, A_n$  in a noncommutative probability space, in such a way that

$$\tau(P(A_1, \dots, A_n)) = \lim_{N \rightarrow \infty} \frac{1}{N} \mathbb{E} \operatorname{tr} P(X_1^{(N)}, \dots, X_n^{(N)}),$$

where  $\mathbb{E}$  stands for probabilistic expectation.

One of the most famous such cases is *Wigner’s theorem*, which asserts that the limiting distribution of large Hermitian matrices with independent Gaussian entries is the so-called semi-circular law.

Voiculescu had the following idea: Let  $A_1, \dots, A_n$  be any  $n$ -tuple of self-adjoint operators, why not try to think of  $\tau = \operatorname{law}(A_1, \dots, A_n)$  as the observable limit of a family of large matrices? In a statistical physics perspective, the operators  $A_i$  would represent some kind of macroscopic system, and the large matrices would be the microscopic system. This led him to the following definitions:

$$\begin{aligned} \Omega(N, \varepsilon, k) &:= \left\{ (X_1, \dots, X_n), N \times N \text{ Hermitian; for all polynomials } P \text{ of} \right. \\ &\quad \left. \text{degree } \leq k: \left| \frac{1}{N} \operatorname{tr} P(X_1, \dots, X_n) - \tau(P(A_1, \dots, A_n)) \right| < \varepsilon \right\}; \\ \chi(\tau) &:= \lim_{k \rightarrow \infty} \limsup_{\varepsilon \rightarrow 0} \limsup_{N \rightarrow \infty} \left[ \frac{1}{N^2} \log \operatorname{vol}(\Omega(N, \varepsilon, k)) - \frac{n}{2} \log N \right] \end{aligned}$$

Once again, behind the abstract framework the reader should recognize Boltzmann’s formula! By lack of competence, I shall not describe the powerful results obtained by Voiculescu thanks to this new tool; but instead reproduce the 2004 quotation of the National Academy of Sciences of USA:

*Award in Mathematics: A prize awarded every four years for excellence in published mathematical research goes to Dan Virgil Voiculescu, professor, department of mathematics, University of California, Berkeley. Voiculescu was chosen “for the theory of free probability, in particular, using random matrices and a new concept of entropy to solve several hitherto intractable problems in von Neumann algebras.”*

What would be Boltzmann's reaction if he were to learn of such an unexpected outcome of his ideas?

## 6 *H* and hydrodynamical limit

The *H*-theorem is one of the main conceptual tools which can make us believe in the *hydrodynamical limit*. Take for instance the Boltzmann equation, in the form

$$\tau \frac{\partial f}{\partial t} + v \cdot \nabla_x f = \frac{1}{\text{Kn}} Q(f, f),$$

where  $\tau$  (time-rescaling) and  $\text{Kn}$  (Knudsen number) are positive parameters. Assume that we are considering small fluctuations around a global equilibrium, and make the ansatz

$$f(t, x, v) = \frac{e^{-|v|^2/2}}{(2\pi)^{3/2}} (1 + \varepsilon g(t, x, v)).$$

As  $\text{Kn}$  becomes very small (physically speaking, this means that the mean free path is very short), the effect of collisions is enhanced, and the finiteness of the entropy production forces  $f$  to be very close to a *local Maxwellian*, that is a state of the form

$$f(x, v) \simeq M_{\rho u T}(x, v) = \rho(x) \frac{e^{-|v - u(x)|^2/2T(x)}}{(2\pi T(x))^{3/2}}.$$

Indeed, it is part of the *H*-theorem that such distributions are the only ones for which the entropy production vanishes.

This approximation by a local Maxwellian imposes a tremendous reduction of the complexity of the description, called *hydrodynamic approximation*.

The mathematical study of the hydrodynamic approximation has a long history; in spite of its loose formulation, it is clear that Hilbert's sixth problem alludes to it (among other things). Many authors have established the validity of the hydrodynamic approximation under various sets of assumptions (with or without smoothness, close to or far from equilibrium, in a compressible or incompressible regime, etc.) Arkeryd, Asano, Bardos, Caflisch, Cercignani, DeMasi, Ellis, Esposito, Golse, Grad, Illner, Lebowitz, Levermore, Lions, Marra, Maslova, Masmoudi, Nishida, Pinsky, Pulvirenti, Romanovski, Saint-Raymond, Ukai, and other researchers contributed to this story.

One spectacular achievement in this class of problems is the *incompressible Navier-Stokes limit in the large*, recently accomplished by Golse and Saint-Raymond [13] (with previous input by Bardos, Golse, Levermore, Lions, Masmoudi). Stated very informally, the main result is as follows. For each  $\varepsilon > 0$ , let  $f_\varepsilon$  solve  $\varepsilon \partial_t f_\varepsilon + v \cdot \nabla_x f_\varepsilon = \frac{1}{\varepsilon} Q(f_\varepsilon, f_\varepsilon)$  in  $[0, T] \times \mathbb{R}^3 \times \mathbb{R}^3$ . Make certain assumptions on the collision kernel, and assume further that

$$H(f_\varepsilon | M) = \int f_\varepsilon \log \frac{f_\varepsilon}{M} dx dv = O(\varepsilon^2).$$

Let  $u_\varepsilon = \frac{1}{\varepsilon} \int f_\varepsilon(x, v) v dv$ . Then any weak cluster point  $u = \lim_{k \rightarrow \infty} (u_{\varepsilon_k})$ , where  $\varepsilon_k \rightarrow 0$ , solves the incompressible Navier–Stokes equation

$$\frac{\partial u}{\partial t} + (u \cdot \nabla) u + \nabla p = \nu \Delta u, \quad \nabla \cdot u = 0$$

for some viscosity coefficient  $\nu > 0$  which depends on the form of Boltzmann's collision kernel.

From the physical point of view, the way to achieve incompressibility is via small perturbations of equilibrium; so the unknown  $u$  is not really a velocity, but rather a fluctuation of velocity (around rest). The time-rescaling is the way to go beyond the short timescale of *sound waves*.

What makes all the beauty of the Golse–Saint-Raymond theorem, and also makes its proof incredibly difficult, is the fact that there is ***no assumption of smoothness or smallness on  $u$*** .

Not surprisingly, entropy and the  $H$ -theorem play a key role in these results. They are used to

- define the notion of convergence:  $H(f|M) = O(\varepsilon^2)$ , where  $H(f|M)$  stands for a natural notion of “relative”  $H$ -function of  $f$  with respect to the equilibrium  $M$ ;
- get the compactness in the limit  $\varepsilon \rightarrow 0$ ;
- prove the hydrodynamic behavior in the limit;
- control the conservation laws asymptotically in the limit. Indeed, the DiPerna–Lions solutions, used in this result, are so weak that there is no reason why they should satisfy the local conservation laws which are at the basis of the hydrodynamic behavior... To circumvent this major difficulty, one shows that the possible departure from hydrodynamic behavior can be controlled by entropic estimates; here is one such inequality due to Golse and Levermore [12]:

$$\left| \int \frac{Q(f, f)}{1 + (f/M)} |v|^2 dv \right| \leq C (H(f|M) + D(f) + 1).$$

There seems to be no physical intuition for this last use of the entropy estimates; we can appreciate on this occasion the versatility of this tool.

## 7 The $H$ -theorem as a source of qualitative macroscopic information

Let us now go back to the Boltzmann equation

$$\frac{\partial f}{\partial t} + v \cdot \nabla_x f = Q(f, f),$$

with fixed physical scales, say in a bounded physical domain.

As already said, when the  $H$ -function does not decrease strictly,  $f$  is ***locally Maxwellian***:

$$f(x, v) = \rho(x) \frac{e^{-\frac{|v-u(x)|^2}{2T(x)}}}{(2\pi T(x))^{3/2}},$$

where  $\rho, u, T$  may depend on  $x$ .

On the other hand, when the  $H$ -function is minimal,  $f$  is **globally** Maxwellian: not only does it take a Maxwellian form, but also the density  $\rho$  and the temperature  $T$  are constant all over the domain, while the velocity is everywhere equal to 0. (This rule admits some exceptions in case of exceptional geometry, but is true for, say, a generic bounded domain in  $\mathbb{R}^2$  or  $\mathbb{R}^3$ , with specular reflection on the boundary.)

These elements suggest that the  $H$ -theorem is a great tool to study relaxation to equilibrium.

An ambitious program about entropy production was started in the early nineties by Carlen–Carvalho and Desvillettes, with some critical impulse by Cercignani (and inspiration from earlier work of McKean). The goal of this program was to *study the large-time behavior of the Boltzmann equation in the large, through the behavior of the  $H$ -function*. One hopes to prove in particular that the solution  $f(t, \cdot)$  approaches a global Maxwellian equilibrium as  $t \rightarrow \infty$ , *keeping a control on time scales!*

A noticeable achievement of this program is the following result due to Desvillettes and myself [9]. It is a conditional result, in the sense that it applies under regularity conditions which in general are still an open problem for the Boltzmann equation:

Let  $f(t, x, v)$  be a solution of the Boltzmann equation, with appropriate boundary conditions. Assume that

(i)  $f$  is very regular (uniformly in time): all moments ( $\int f|v|^k dv dx$ ) are finite and all derivatives (of any order) of  $f$  are bounded;

(ii)  $f$  is strictly positive:  $f(t, x, v) \geq K e^{-A|v|^q}$ .

Then  $f(t, \cdot)$  approaches the unique equilibrium as  $t \rightarrow \infty$ , and the convergence is at least like  $O(t^{-\infty})$  (the distance to equilibrium goes to 0 faster than any inverse power of time).

At present, this theorem applies only in certain particular cases (spatial homogeneity; close-to-equilibrium) because of the limitations of the regularity theory of the Boltzmann equation. What it achieves, in full generality, is a *conversion of regularity bounds into decay bounds*.

The proof of this theorem uses differential inequalities of first and second order, coupled via many inequalities including:

– Precised **entropy production inequalities** (who would have guessed...). For instance, under some strong a priori estimates on  $f$  (smoothness, moments, positivity), one can show that

$$D(f) \geq K_{f,\varepsilon} [H(f) - H(M_{\rho u T}^f)]^{1+\varepsilon}.$$

(This is a modified version of the so-called “Cercignani conjecture” [6], [18], [20].)

– The instability of hydrodynamical description: for instance we show that

$$\begin{aligned} & \frac{d^2}{dt^2} \left( \int (f - M_{\rho u T}^f)^2 \right) \\ & \geq K \int_{\Omega} (|\nabla_x T|^2 + |\text{dev}(u)|^2) dx - C_{\varepsilon}(f) \|f - M_{\rho u T}^f\|_{L^2}^{1-\varepsilon} H(f|M)^{\frac{1-\varepsilon}{2}}, \end{aligned}$$

where  $M_{\rho u T}^f$  stands for the local Maxwellian with same density  $\rho$ , velocity  $u$  and temperature  $T$  as  $f$ ; and  $\text{dev}$  is the deviatoric part of  $u$ , i.e. the traceless symmetric part of the Reynolds tensor  $\nabla u$ .

Such inequalities mean that if  $f$  becomes very close to a hydrodynamic state, then the time-evolution of the (squared) distance between  $f$  and the set of hydrodynamical states will evolve in a convex manner, and therefore  $f$  will depart from hydrodynamic behavior.

Another key feature of the proof is the fact that entropy sees both kinetic and hydrodynamic effects. Indeed, it can be separated into a “purely kinetic” and a “purely hydrodynamic” contributions:  $H(f) - H(M) = [H(f) - H(M_{\rho u T}^f)] + \mathcal{H}(\rho, u, T)$ , where  $\mathcal{H}(\rho, u, T) = \int_{\Omega} \rho \log \frac{\rho}{T^{3/2}} dx$ .

A careful study of the proof led Desvillettes and myself to conjecture the existence of strong time-oscillations in the entropy production. These oscillations were spectacularly confirmed in numerical simulations by Francis Filbet (see figures below), and are currently being studied, both numerically and theoretically [11].

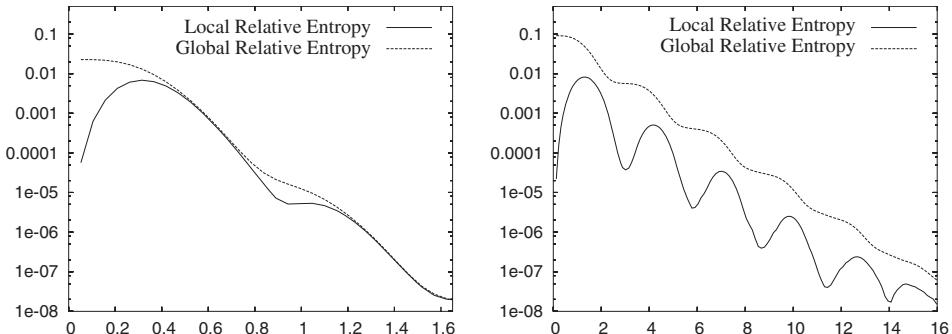


Figure 1. Time-decay of the  $H$ -function, in logarithmic scale, for the Boltzmann equation in one dimension of space and two dimensions of velocity, with periodic boundary conditions. The curve above is the  $H$ -function, the curve below is the purely kinetic part of the  $H$ -function; when the two curves are far from each other the gas is almost hydrodynamical, when they are close to each other it is almost homogeneous.

More information about the history and achievements of the subject can be found in the proceedings of the 2003 International Congress of Mathematical Physics [21], or in a course which I taught at the Institut Henri Poincaré [22].

## 8 More on the qualitative behavior of the entropy

The importance and flexibility of Boltzmann’s  $H$ -function as a way to describe the qualitative behavior of a system goes much beyond the field of partial differential equations. In the last two sections of this text I shall illustrate this by two examples: (a) the central limit theorem in probability theory; (b) Ricci curvature bounds in Riemannian geometry.

## 9 The central limit theorem

Let  $X_1, X_2, \dots, X_n, \dots$  be identically distributed, independent real random variables; assume that  $\mathbb{E}X_j^2 < \infty$ ,  $\mathbb{E}X_j = 0$ . Then

$$\frac{X_1 + \dots + X_N}{\sqrt{N}} \xrightarrow[N \rightarrow \infty]{} \text{Gaussian random variable.}$$

This is the central limit theorem which we learn in basic probability courses.

A few years ago, Ball, Barthe and Naor [3] interpreted this as an *irreversible loss of information* along the sequence of random variables; namely,

$$\text{Entropy} \left( \frac{X_1 + \dots + X_N}{\sqrt{N}} \right) \text{ increases with } N.$$

(Weaker versions of this theorem, involving only powers of 2, had been proven before by Barron; and Carlen–Soffer.)

This “entropic” proof of the central limit theorem is very different from the usual proof based on Fourier transform; it is also much more complicated. Still it gives an information-theoretical interpretation of the central limit theorem which Boltzmann certainly would have appreciated very much.

## 10 $H$ -function and Ricci curvature

My last example will lead me into differential geometry. The Ricci curvature is (together with the sectional and scalar curvatures) one of the three most popular notions of curvature. If  $M$  is a Riemannian manifold, then the Ricci curvature  $\text{Ric}_x$  at  $x$  is a quadratic form on  $T_x M$ .

A quick (albeit incomprehensible) definition of the Ricci curvature is by contraction of the Riemann curvature tensor:  $(\text{Ric})_{ij} = (\text{Riem})_{kij}^k$ . Intuitively, the Ricci curvature measures the rate of separation of geodesics in a given direction, *in the sense of volume* (Jacobian). As usual, positive curvature indicates a tendency for geodesics to converge, while negative curvature indicates a tendency to diverge faster than in Euclidean space.

A more hand-on approach to Ricci curvature bounds is in terms of distortion coefficients. For instance, it is equivalent to say that the Ricci curvature of a Riemannian manifold  $M$  is nonnegative; or that its distortion coefficients are never less than 1, i.e. one always overestimates the surface of observed light sources (see Figure 2).

Lower bounds on Ricci curvature are of constant use in Riemannian geometry: they appear as privileged assumptions for isoperimetric inequalities; heat kernel estimates; Sobolev inequalities; diameter control; spectral gap inequalities; upper bounds on the volume growth; compactness criteria for families of manifolds; etc.

The following theorem was proven independently by Lott and me [14], and by Sturm [17]:

*A limit of manifolds with nonnegative Ricci curvature, is also of nonnegative curvature.*

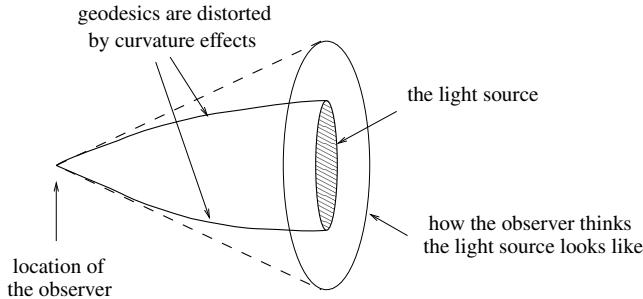


Figure 2. Because of positive curvature effects, the observer overestimates the surface of the light source.

This theorem is interesting because the notion of limit used is a very weak one, namely the measured Gromov–Hausdorff topology; and there is no reason why the Ricci tensor would pass to the limit in the process. The limit might even occur with a reduction of dimension (collapsing); in which case one has to use a slightly more intrinsic notion of Ricci curvature allowing for a change of reference measure.

Since I mention this theorem in this lecture, the reader has probably guessed that its proof uses Boltzmann’s entropy! And indeed the proof of the theorem does rely on entropy, in relation with the ***optimal transport of probability measures***, along a direction of research developed by various authors (Cordero-Erausquin, Lott, McCann, Otto, von Renesse, Schmuckenschläger, Sturm, and myself).

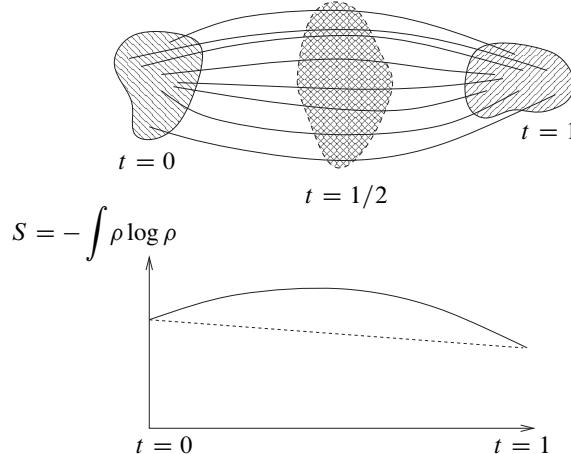


Figure 3. The lazy gas experiment: To go from initial state to final state, the lazy gas uses a path of least action. In a nonnegatively curved world, the trajectories of particles first diverge, then converge, so that at intermediate times the gas can afford to have a lower density (higher entropy).

To explain this connection I shall describe what I call the *lazy gas experiment*.

Take a perfect gas in which particles do not interact, and ask it to move from a certain prescribed density field at time  $t = 0$ , to another prescribed density field at time  $t = 1$ . Since the gas is lazy, it will find a way to do so by spending a minimal amount of work (least action path). Measure the entropy of the gas at each time, and check that it always lies *above* the line joining the final and initial entropies. If such is the case, then we know that we live in a nonnegatively curved space.

Of course these heuristics do not explain why the entropy is precisely the relevant functional to measure the concentration of the gas; this prediction was made by Otto and myself in 2000 [15], after a study of relations between optimal transport, logarithmic Sobolev inequalities and the entropy functional. In the reference book [23] I explain all this and much much more; still I remain marvelled by this new role of Boltzmann's ubiquitous entropy.

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*Über die Grundprinzipien und Grundgleichungen der Mechanik*

Drawing by Karl Przibram

(Courtesy of the Österreichische Zentralbibliothek für Physik)

# On the Boltzmann equation for weakly nonlinear wave equations

Herbert Spohn

## Introduction

Kinetic theory is an everlasting contribution of Ludwig Boltzmann to physics. While he devised the theory to understand the dynamics of dilute gases, the method as such is much more general and has been applied with great success in many areas. A more recent example is the flow of granular media. Their defining property are inelastic collisions. Thus a natural, in fact highly informative, approach is to follow the route of kinetic theory, adjusting for the appropriate collision mechanism [1].

In the early days of kinetic theory it was a convoluted process to understand that the Boltzmann equation cannot possibly hold for every mechanical initial condition. But to set forward the proposition that the Boltzmann equation becomes exact in a particular limiting procedure, now called the Boltzmann-Grad limit [2], took almost 80 years counted from Boltzmann's 1872 paper. In this limit the sometimes painfully vague notions of "overwhelming probability" and the like acquire a definite meaning. For example, the set of exceptional initial phase points has a measure (w.r.t. the initial measure on phase space) which tends to zero in the Boltzmann-Grad limit. Grad's proposition was proved as a mathematical theorem by Lanford [3], see [4], [5] for more expanded discussions.

Given the example of low density gases, one might wonder whether similar ideas are applicable to further microscopic systems. The Landau equation for weakly interacting particles and the Vlasov equation for weak, long range forces are examples from plasma physics. After the advent of quantum mechanics, an obvious task was to also adjust kinetic theory. In a pioneering work Nordheim [6] guessed the appropriate generalization, both for Bose-Einstein and Fermi-Dirac statistics. A more systematic derivation was accomplished by Peierls [7] for the case of quantized lattice vibrations (phonons). Uehling and Uhlenbeck [8] studied the long time behavior of the respectively generalized Boltzmann equations.

The derivation of the Boltzmann equation for interacting quantum particles is well covered in recent articles [9], [10], [11]. Here I summarize the current status for weakly nonlinear wave equations with random initial data. On the surface this problem looks simpler than weakly interacting quantum particles, since there is no need for operators, Fock spaces, and the like. On the other hand, at least on the level of time-dependent perturbation theory, the wave equation and quantum systems have similar Feynman diagrams. In particular cases the wave diagrams are a proper subset of the set of all quantum diagrams. As a consequence the limiting kinetic equations differ only minimally. For the kinetic description a dividing line seems to be point particles versus wave equation, the latter case being much less understood because of the nonlocal

interaction once the dynamics is expressed in terms of multi-point Wigner functions.

Writing down a kinetic equation always involves some modeling aspects. The available experience provides sufficient guidance as to what would constitute an acceptable kinetic equation. There is then no point in waiting for a firm microscopic derivation. Rather more urgently is to work out predictions from the kinetic equation, which by itself is a demanding endeavour. In fact, a kinetic equation to be exact in a particular limit might very well be exceptional. A prominent example are lattice Boltzmann algorithms, which are used widely to simulate flows in complicated geometries and close to reacting surfaces. For such algorithms the Boltzmann equation remains as an approximation, although a very powerful one.

To give a brief outline, in the following section we explain, what I call, the kinetic framework. Physicists tend to be more computationally oriented and the underlying statistical properties of the microscopic system are rarely spelled out in full detail. But on a conceptual level the kinetic framework is most useful and, assuming it to hold, the kinetic equation is obtained rather easily. We emphasize that the kinetic framework is not restricted to a particular model. It is a general structure, which can be used whenever a splitting into a “free” part and an appropriately small perturbation is meaningful. In Section 2 we write down the phonon Boltzmann equation in case of a quartic potential. Some of the basic properties of this equation are discussed in Section 3. Perhaps somewhat unexpected, the kinetic approach yields interesting dynamical information even for an anharmonic chain. In this light we revisit the famous Fermi–Pasta–Ulam problem.

## 1 The kinetic framework

We plan to study the scalar wave equation in three space dimensions with a cubic nonlinearity of the form

$$\frac{\partial^2}{\partial t^2}u = \Delta u - \sqrt{\lambda}u^3. \quad (1.1)$$

Here  $u : \mathbb{R} \times \mathbb{R}^3 \rightarrow \mathbb{R}$  is the wave field,  $\Delta$  the Laplacian, and  $\lambda > 0$ , but small. The initial data are random and of finite energy. As will be explained, the total energy is taken to be of order  $\lambda^{-3}$  and the support of  $u$  of linear extent  $\lambda^{-1}$ . To avoid the issue of ultraviolet divergencies, equation (1.1) is discretized spatially through the standard grid  $\mathbb{Z}^3$ . It is important to also allow for a general dispersion relation of the linear part. Physically, the discretized wave equation describes the lattice dynamics of dielectric crystals, see [12], [13], [14] for systematic expositions. In this context the scalar equation would correspond to a one-band approximation.

Fourier transform will be a convenient tool. Let  $\mathbb{T}^3 = [-\frac{1}{2}, \frac{1}{2}]^3$  be the first Brillouin zone of the lattice dual to  $\mathbb{Z}^3$ . For  $f : \mathbb{Z}^d \rightarrow \mathbb{R}$  its Fourier transform,  $\hat{f}$ , is defined by

$$\hat{f}(k) = \sum_{x \in \mathbb{Z}^3} e^{-i2\pi k \cdot x} f_x. \quad (1.2)$$

Here  $k \in \mathbb{T}^3$  and  $\hat{f}$  extends periodically to a function on  $\mathbb{R}^3$ . The inverse Fourier transform is given by

$$f_x = \int_{\mathbb{T}^3} dk e^{i2\pi k \cdot x} \hat{f}(k). \quad (1.3)$$

For  $x \in \mathbb{Z}^3$  the displacement away from  $x$  is denoted by  $q_x \in \mathbb{R}$  and the corresponding momentum by  $p_x \in \mathbb{R}$ . In the harmonic approximation the interaction potential is

$$U_{\text{harm}}(q) = \frac{1}{2} \sum_{x,y \in \mathbb{Z}^3} \alpha(x-y) q_x q_y. \quad (1.4)$$

The elastic constants  $\alpha(x)$  satisfy

$$\alpha(x) = \alpha(-x) \quad \text{and} \quad |\alpha(x)| \leq \gamma_0 e^{-\gamma_1 |x|} \quad (1.5)$$

for suitable  $\gamma_0, \gamma_1 > 0$ . Mechanical stability requires

$$\hat{\alpha}(k) \geq 0. \quad (1.6)$$

In fact, we assume  $\hat{\alpha}(k) > 0$  for  $k \neq 0$ . The case  $\hat{\alpha}(k) \simeq k^2$  for small  $k$  is referred to as ‘acoustical’ while  $\hat{\alpha}(0) > 0$  is ‘optical’. The dispersion relation of the harmonic part is

$$\omega(k) = \sqrt{\hat{\alpha}(k)}. \quad (1.7)$$

Following (1.1) as a concrete example, we consider a quartic on-site potential. Then the full hamiltonian of the lattice dynamics is given by

$$H = \frac{1}{2} \sum_{x \in \mathbb{Z}^3} p_x^2 + \frac{1}{2} \sum_{x,y \in \mathbb{Z}^3} \alpha(x-y) q_x q_y + \frac{1}{4} \sqrt{\lambda} \sum_{x \in \mathbb{Z}^3} q_x^4. \quad (1.8)$$

The harmonic part of  $H$  will be denoted by  $H_{\text{ha}}$ ,  $H = H_{\text{ha}} + \sqrt{\lambda} V$ . In a sense to be explained below,  $\sqrt{\lambda} V$  is a “small” perturbation of  $H_{\text{ha}}$ .

We concatenate  $q_x$  and  $p_x$  into a single complex-valued field  $a(k)$  as

$$a(k) = \frac{1}{\sqrt{2}} \left( \sqrt{\omega(k)} \hat{q}(k) + i \frac{1}{\sqrt{\omega(k)}} \hat{p}(k) \right) \quad (1.9)$$

with the inverse

$$\hat{q}(k) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{\omega(k)}} (a(k) + a(-k)^*), \quad \hat{p}(k) = \frac{i}{\sqrt{2}} \sqrt{\omega(k)} (-a(k) + a(-k)^*). \quad (1.10)$$

Then the hamiltonian reads

$$H = H_{\text{ha}} + \sqrt{\lambda} V, \quad H_{\text{ha}} = \int_{\mathbb{T}^3} dk \omega(k) a(k)^* a(k), \quad (1.11)$$

$$V = \frac{1}{4} \int_{\mathbb{T}^{12}} dk_1 dk_2 dk_3 dk_4 \delta(k_1 + k_2 + k_3 + k_4) \\ \times \prod_{j=1}^4 (2\omega(k_j))^{-1/2} (a(k_j) + a(-k_j)^*). \quad (1.12)$$

Hence the equations of motion for the  $a$ -field are

$$\frac{\partial}{\partial t} a(k, t) = -i\omega(k)a(k, t) - i\sqrt{\lambda} \int_{\mathbb{T}^9} dk_1 dk_2 dk_3 \delta(k - k_1 - k_2 - k_3) \\ \times (2\omega(k))^{-1/2} \prod_{j=1}^3 (2\omega(k_j))^{-1/2} (a(k_j, t) + a(-k_j, t)^*). \quad (1.13)$$

In particular for  $\lambda = 0$ ,

$$a(k, t) = e^{-i\omega(k)t} a(k). \quad (1.14)$$

Let us now briefly recall the case of dilute gases. The central quantity is the Boltzmann  $f$ -function, which is the number density on one-particle phase space  $\mathbb{R}^3 \times \mathbb{R}^3$ . It changes in time by the free motion of particles and through pair collisions,

$$\frac{\partial}{\partial t} f_t + v \cdot \nabla_r f_t = \mathcal{C}(f_t, f_t). \quad (1.15)$$

We do not write out the collision operator explicitly but note that it is bilinear in  $f_t$  and strictly local in the space-variable  $r$ , since on the kinetic scale particles collide at the same point. At low density the full particle statistics is close to Poisson, jointly in positions and velocities, with an intensity given again by the  $f$ -function. This double meaning of the  $f$ -function is a source of conceptual confusion. In the Stößzahlansatz one assumes independent incoming velocities, thus the second meaning of  $f$ , while the predictions of kinetic theory are based on a law of large numbers, thus the first meaning of  $f$ . The Poisson statistics appears naturally through the good statistical mixing properties of the collisionless dynamics. In fact, at infinite volume, these are the only translation invariant measures, which are invariant under the collisionless dynamics and which have a finite number, energy, and entropy per unit volume [15].

For wave equations the Poisson measure will be substituted by a Gaussian measure, constrained to be locally invariant under the dynamics generated by  $H_{\text{ha}}$ . In the *spatially homogeneous* case, imposing time-stationarity and using the explicit solution (1.14) for  $\lambda = 0$ , the  $\{a(k), k \in \mathbb{T}^3\}$  are then jointly Gaussian with mean zero and covariance

$$\langle a(k)^* a(k') \rangle = W(k) \delta(k - k'), \quad (1.16)$$

$$\langle a(k)^* a(k')^* \rangle = 0, \quad \langle a(k) a(k') \rangle = 0, \quad (1.17)$$

defining the power spectrum  $W(k)$ . Clearly,  $W(k) \geq 0$ .

For the *spatially inhomogeneous* case the construction is slightly more elaborate. Since the anharmonic potential is of order  $\sqrt{\lambda}$ , the mean free path for phonons is of order  $\lambda^{-1}$ . This is the scale on which spatial inhomogeneities have to be imposed.

Local stationarity still implies mean zero and (1.17). For the covariance (1.16) we first prescribe the limiting local power spectrum  $W: \mathbb{R}^3 \times \mathbb{T}^3 \rightarrow \mathbb{R}$  with  $W \geq 0$  and a rapid decay in position space. In analogy to the semiclassical limit of the Schrödinger equation we refer to  $W$  as Wigner function. A *locally stationary* Gaussian measure, denoted by  $\langle \cdot, \cdot \rangle^{G,\lambda}$ , is in fact a scale of probability measures depending on  $\lambda$ . For each  $\lambda$  the measure  $\langle \cdot, \cdot \rangle^{G,\lambda}$  is Gaussian with

$$\langle a(k) \rangle^{G,\lambda} = 0, \quad \langle a(k)a(k') \rangle^{G,\lambda} = 0. \quad (1.18)$$

Following Wigner the local power spectrum of the  $a$ -field is defined through

$$P^1(x, k) = 2^{-3} \int_{(2\mathbb{T})^3} d\eta e^{i2\pi x \cdot \eta} a(k - \eta/2)^* a(k + \eta/2). \quad (1.19)$$

We rescale the lattice to have lattice spacing  $\lambda$  through the substitution  $x = \lambda^{-1}y$ ,  $y \in (\lambda\mathbb{Z}/2)^3$ , and obtain the rescaled local power spectrum

$$P^\lambda(y, k) = (\lambda/2)^3 \int_{(2\mathbb{T}/\lambda)^3} d\eta e^{i2\pi y \cdot \eta} a(k - \lambda\eta/2)^* a(k + \lambda\eta/2). \quad (1.20)$$

$P^\lambda$  is a random field. By definition, its average is the one-particle Wigner function,

$$W_1^\lambda(y, k) = \langle P^\lambda(y, k) \rangle^{G,\lambda} \quad (1.21)$$

and its variance the two-particle Wigner function,

$$W_2^\lambda(y_1, k_1, y_2, k_2) = \langle P^\lambda(y_1, k_1) P^\lambda(y_2, k_2) \rangle^{G,\lambda}. \quad (1.22)$$

With  $\lfloor \cdot \rfloor_\lambda$  denoting modulo  $\lambda$ , the scale of Gaussian measures  $\langle \cdot, \cdot \rangle^{G,\lambda}$  is assumed to satisfy the pointwise limit

$$\lim_{\lambda \rightarrow 0} W^\lambda(\lfloor r \rfloor_\lambda, k) = W(r, k). \quad (1.23)$$

Furthermore one has to require a law of large numbers for the power spectrum  $P^\lambda$  which can be expressed in the form

$$\lim_{\lambda \rightarrow 0} W_2^\lambda(\lfloor r_1 \rfloor_\lambda, k_1, \lfloor r_2 \rfloor_\lambda, k_2) = W(r_1, k_1) W(r_2, k_2) \quad (1.24)$$

for  $r_1 \neq r_2$ .

In general, the assumption of strict Gaussianity is too strong. Because of the anharmonicity, unavoidably there will be small errors. To allow for them we call an arbitrary sequence of probability measures,  $\langle \cdot, \cdot \rangle^\lambda$ , *locally stationary*, if the Gaussian property is gained only in the limit  $\lambda \rightarrow 0$ . More precisely, for our model we may assume that all odd moments of  $\langle \cdot, \cdot \rangle^\lambda$  vanish, since this property is propagated in time. For the second moments  $\langle a(k)a(k') \rangle^\lambda$ ,  $\langle a(k)^*a(k') \rangle^\lambda$  we form the rescaled one-particle Wigner function as in (1.20), (1.21). The rescaled Wigner function for  $\langle a(k)a(k') \rangle^\lambda$  is assumed

to vanish as  $\lambda \rightarrow 0$ , while the rescaled Wigner function for  $\langle a(k)^* a(k') \rangle^\lambda$  satisfies (1.23). (1.24) is imposed correspondingly. In addition we require that the sequence of local measures, close to  $\lambda^{-1} r$  [lattice units], converges to a Gaussian measure with covariance (1.16), (1.17) and  $W(k)$  replaced by  $W(r, k)$ .

From (1.23) we infer that for a locally stationary measure it holds

$$\langle H_{\text{ha}} \rangle^\lambda = \int_{\mathbb{T}^3} dk \omega(k) \langle a(k)^* a(k) \rangle^\lambda = \mathcal{O}(\lambda^{-3}). \quad (1.25)$$

The harmonic energy is extensive. On the other hand the average anharmonic potential satisfies  $\sqrt{\lambda} \langle V \rangle^\lambda = \sqrt{\lambda} \mathcal{O}(\lambda^{-3})$ , which is small compared to  $\langle H_{\text{ha}} \rangle^\lambda$ .

Our real goal is to understand the time evolution in the limit of small  $\lambda$ . We impose the initial measure to be Gaussian and locally stationary. As a simple, but useful first step we set  $V = 0$  and, for a short intermediate stretch only, consider the linear dynamics generated by  $H_{\text{ha}}$ . By linearity this dynamics preserves the Gaussian property. Since the initial state has a slow variation on the scale  $\lambda^{-1}$ , the limit  $\lambda \rightarrow 0$  for the one-particle Wigner function is a particular case of the semiclassical limit for a linear wave equation. Thus the appropriate time scale is also of order  $\lambda^{-1}$  and on that scale

$$\lim_{\lambda \rightarrow 0} W^\lambda(\lfloor r \rfloor_\lambda, k, \lambda^{-1} t) = W(r, k, t). \quad (1.26)$$

(On the left hand side  $\lambda^{-1} t$  is the time in microscopic units, the units of (1.13), while on the right hand side  $t$  refers to kinetic times, the units for (1.15)). The limit Wigner function is governed by the transport equation

$$\frac{\partial}{\partial t} W(r, k, t) + \frac{1}{2\pi} \nabla_k \omega(k) \cdot \nabla_r W(r, k, t) = 0, \quad (1.27)$$

which corresponds to the free motion of fictitious particles, the phonons, with kinetic energy  $\omega$ . Of course, (1.27) has to be solved with the initial condition  $W(r, k, 0) = W(r, k)$ .

We refer to [16], [17] for a complete coverage of the semiclassical limit for lattice dynamics with an arbitrary unit cell. Random initial data are studied in [18], where only rather mild mixing conditions on the initial measure  $\langle \cdot, \cdot \rangle^\lambda$  are imposed. Let  $\langle \cdot, \cdot \rangle_t^\lambda$  be the measure at time  $t$  as evolved according to the dynamics generated by  $H_{\text{ha}}$ . It is proved that for any  $t > 0$  the sequence of measures  $\langle \cdot, \cdot \rangle_{\lambda^{-1}t}^\lambda$  is locally stationary with a Wigner function satisfying the transport equation (1.27). In this sense local stationarity is dynamically generated. Such results require, as does the kinetic limit, that phonons propagate with nonzero velocity. To say one has to demand that  $\nabla_k \omega \neq 0$  a.s. By our assumption,  $\omega^2$  is real analytic on  $\mathbb{T}^3$  and one only has to exclude the case  $\omega = \text{const}$ . Nevertheless, since momentum space is  $\mathbb{T}^3$ , there will always be submanifolds where  $\nabla_k \omega = 0$ , which sets an extra technical difficulty.

We return to the case of interest, namely adding the anharmonicity  $\sqrt{\lambda} V$ . Then, if as before the initial measure is required to be Gaussian and locally stationary, the time-evolved measure  $\langle \cdot, \cdot \rangle_t^{G,\lambda}$  is no longer Gaussian. On the other hand, the linear

dynamics does not tolerate deviations from Gaussianity, as demonstrated in [18], and the strength of the anharmonicity is taken to be small. Thus the family  $\langle \cdot, \cdot \rangle_{\lambda=1}^{G,\lambda}$  is still locally stationary. Of course now  $W(k)$  depends on  $r$  and  $t$  [kinetic scale]. The precise strength of the anharmonic on-site potential is adjusted such that its effect is of order 1 for the scale on which (1.27) holds. More physically speaking, the interaction strength is such that the phonon mean free path is of order  $\lambda^{-1}$  [lattice units]. Thus one expects the limit (1.26) still to be valid. Only the transport equation picks up a term resulting from the collisions between phonons.

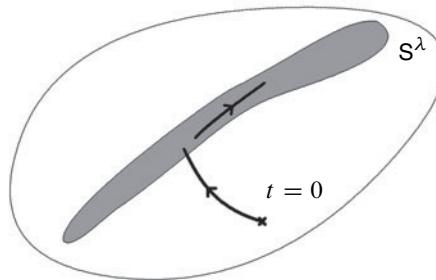


Figure 1. Time evolution of a probability measure under kinetic scaling.

We summarize the kinetic framework by means of a somewhat schematic diagram. The encircled set is supposed to represent the set of “all” probability measures for the random field  $a(k)$ . We fix the interaction strength as  $0 < \lambda \ll 1$ . The manifold-like set denoted by  $S^\lambda$  is the set of all locally stationary measures up to some  $\lambda$ -dependent scale of precision. The hamiltonian dynamics generates a flow on the space of measures. The set  $S^\lambda$  is attractive, in the sense that fairly rapidly, times of order 1, the measure will be close to  $S^\lambda$ . On  $S^\lambda$  the time evolution is slow with changes on the kinetic scale  $\mathcal{O}(\lambda^{-1})$  and the defining Wigner function is governed by a kinetic equation. For  $t \gg \lambda^{-1}$  further dynamical phenomena set in which cannot be captured through the kinetic framework.

## 2 The Boltzmann equation

The kinetic framework provides us with a tool for an educated guess on the form of the collision operator. An important check will be that the resulting equation has the physically correct stationary solutions and satisfies an  $H$ -theorem for the total entropy, respectively a local semi-conservation law with a positive entropy production.

A more demanding issue is to support the educated guess by mathematical arguments which establish the assumed existence of limits and local stationarity.

Let  $\langle \cdot, \cdot \rangle_t^{G,\lambda} = \langle \cdot, \cdot \rangle_t$  denote the measure at time  $t$  under the dynamics generated

by  $H$  with  $\langle \cdot, \cdot \rangle_0 = \langle \cdot, \cdot \rangle^{G, \lambda}$ . The two-point function satisfies

$$\frac{d}{dt} \langle a(p)^* a(q) \rangle_t = i(\omega(p) - \omega(q)) \langle a(p)^* a(q) \rangle_t + \sqrt{\lambda} F(q, p, t). \quad (2.1)$$

$F$  is cubic in the  $a$ -field. We integrate (1.13) in time, symbolically

$$a(t) = e^{-i\omega t} a + \sqrt{\lambda} \int_0^t e^{-i\omega(t-s)} a(s)^3, \quad (2.2)$$

and insert (2.2) in the expression for  $F$ . There are then cubic terms, proportional to  $\sqrt{\lambda}$ , which vanish upon averaging, and sixtic terms, proportional to  $\lambda$ . At this point we use, as argued, that locally the measure is approximately Gaussian and factorize the 6-point function according to the Gaussian rule for moments. We also rescale space-time by  $\lambda^{-1}$  and switch to Wigner function coordinates. In this form one can take the limit  $\lambda \rightarrow 0$ . The first term on the right of (2.1) yields the free flow while  $\sqrt{\lambda} F$  results in the collision operator with a cubic nonlinearity.

Details of such computations are provided by Erdős, Salmhofer, Yau [9], and in [19]. Here we only quote the result, which is the Boltzmann equation

$$\frac{\partial}{\partial t} W(r, k, t) + \frac{1}{2\pi} \nabla_k \omega(k) \cdot \nabla_r W(r, k, t) = \mathcal{C}(W(r, t))(k). \quad (2.3)$$

The collision operator is local in  $r, t$ , which our notation is supposed to indicate.  $\mathcal{C}$  is a nonlinear functional of  $k \mapsto W(r, k, t)$  at fixed  $r, t$ . For the quartic on-site potential,  $\mathcal{C}$  is cubic and defined through

$$\begin{aligned} \mathcal{C}(W)(k) = 12\pi & \sum_{\sigma_1, \sigma_2, \sigma_3 = \pm 1} \int_{\mathbb{T}^9} dk_1 dk_2 dk_3 (16\omega\omega_1\omega_2\omega_3)^{-1} \\ & \times \delta(k + \sigma_1 k_1 + \sigma_2 k_2 + \sigma_3 k_3) \delta(\omega + \sigma_1\omega_1 + \sigma_2\omega_2 + \sigma_3\omega_3) \\ & \times (W_1 W_2 W_3 + W(\sigma_1 W_2 W_3 + W_1 \sigma_2 W_3 + W_1 W_2 \sigma_3)), \end{aligned} \quad (2.4)$$

where we use the shorthand  $W_j = W(k_j)$ ,  $\omega_j = \omega(k_j)$ ,  $j = 1, 2, 3$ . The term proportional to  $W$  is the loss term. It has no definite sign. On the other hand the gain term  $W_1 W_2 W_3$  is always positive, ensuring that the positivity of the initial Wigner function is propagated in time.

As a historical parenthesis we remark that in his seminal paper Peierls uses a very different reasoning. The current method goes back to the mid-fifties where Green's function techniques were developed systematically along the lines set forth by quantum field theory. The textbook expositions of the phonon Boltzmann equation are not so satisfactory, at least in solid state physics. For the quantized theory Fermi's golden rule is applied in a spatially homogeneous, discrete mode context. While this gives the correct collision operator, the 'why' remains obscure. Classical lattice dynamics is conceived only as a  $\hbar \rightarrow 0$  limit of the quantum theory. The situation is more favorable in wave turbulence, where the starting point is a weakly nonlinear system of

wave equations in hamiltonian form [20]. Statistical properties are accessible and the validity of Gaussian statistics is an important issue [21], [22].

At present, we are very far away from a complete mathematical proof of the existence of the limit in equation (1.26) together with the property that the limiting Wigner function is the solution to (2.3), (2.4) with initial conditions  $W(r, k, 0) = W(r, k)$ . Apparently, the only available technique is to expand with respect to  $\sqrt{\lambda}V$  into a time-dependent perturbation series. Each term of the series can be represented symbolically as a Feynman diagram, which represents an oscillatory integral. In the limit  $\lambda \rightarrow 0$  most diagrams vanish (subleading diagrams) and a few do not vanish (leading diagrams). The sum over all leading diagrams yields the time-dependent perturbation series of the Boltzmann equation, where the free flow is integrated and the collision term is regarded as perturbation. The conjectured division into leading and subleading diagrams is explained in [23].

The program outlined has been carried out only fragmentarily. The first order, proportional to  $\sqrt{\lambda}$ , vanishes. To second order one expects the limit

$$\int_0^t ds e^{L(t-s)} \mathcal{C}(e^{Ls} W), \quad (2.5)$$

where  $(e^{Lt} W)(r, k) = W(r - (2\pi)^{-1} \nabla_k \omega(k)t, k)$ . While such limit could be established at the level of generality discussed here, even this point has not be accomplished. Closest to the goal comes the very careful analysis of Ho and Landau [24], who study the same problem for a weakly interacting Fermi liquid on  $\mathbb{Z}^3$  with nearest neighbor hopping and obtain the analogue of (2.5). Benedetto, Castella, Esposito and Pulvirenti [25], [26] consider a weakly interacting quantum fluid in  $\mathbb{R}^3$  with the usual kinetic energy  $p^2/2m$ . In our context this would correspond to the nonlinear Schrödinger equation,  $m = 1$ ,

$$i \frac{\partial}{\partial t} \psi(x, t) = \left( -\frac{1}{2} \Delta_x + \sqrt{\lambda} V_\psi(x, t) \right) \psi(x, t) \quad (2.6)$$

with the effective potential

$$V_\psi(x, t) = \int_{\mathbb{R}^3} dy \vartheta(x - y) |\psi(y, t)|^2. \quad (2.7)$$

$\vartheta$  smoothens the interaction on a microscopic scale. The role of the  $a$ -field is taken over by the Fourier transform  $\hat{\psi}$ . The Wigner function  $W^\lambda(t)$  is precisely the standard Wigner function for the Schrödinger equation at time  $\lambda^{-1}t$  averaged over the initial Gaussian distribution of the  $\psi$ -field. The Boltzmann equation for the nonlinear Schrödinger equation (2.6) has the same overall structure as (2.3), (2.4). More precisely, now  $k \in \mathbb{R}^3$  and

$$\frac{\partial}{\partial t} W(r, k, t) + k \cdot \nabla_r W(r, k, t) = \mathcal{C}_{\text{NS}}(W(r, t))(k) \quad (2.8)$$

with the collision operator

$$\begin{aligned} \mathcal{C}_{\text{NS}}(W)(k_1) = & 12\pi \int_{\mathbb{R}^9} dk_2 dk_3 dk_4 |\hat{\vartheta}(k_1 - k_2)|^2 2\delta(k_1^2 + k_2^2 - k_3^2 - k_4^2) \\ & \times \delta(k_1 + k_2 - k_3 - k_4) (W_2 W_3 W_4 - W_1 (W_2 W_3 + W_2 W_4 - W_3 W_4)). \end{aligned} \quad (2.9)$$

The Feynman diagrams of the nonlinear Schrödinger equation are a proper subset of those investigated in [25]. Using their result, one concludes that in the limit  $\lambda \rightarrow 0$  the second order expansion term is given by (2.5) with the appropriate adjustments for  $L$  and  $\mathcal{C}$ .

### 3 Stationary solutions, entropy production

For dilute gases the  $f$ -function derived from the thermal equilibrium distribution of the  $N$ -particle system is a stationary solution of the kinetic equation. If one identifies the entropy with the logarithm of phase space volume associated to some given  $f$ -function on one-particle phase space, then the entropy functional turns out to be

$$S(f) = - \int dv f(v) \log f(v), \quad (3.1)$$

in units where Boltzmann's constant  $k_B = 1$ .  $S(f)$  is increasing in time and constant if and only if  $f$  is Maxwellian (at least in the spatially homogeneous case). Thus the reader may wonder whether the phonon Boltzmann equation has similar properties.

To determine the collision rule for phonons, one has to solve the conservation laws of energy and momentum, see equation (2.4). For pair collisions, i.e.  $\sum_{j=1}^3 \sigma_j = -1$ , this amounts to

$$\omega(k_1) + \omega(k_2) = \omega(k_3) + \omega(k_1 + k_2 - k_3) \quad (3.2)$$

and for three phonons mergers to

$$\omega(k_1) + \omega(k_2) + \omega(k_3) = \omega(k_1 + k_2 + k_3), \quad (3.3)$$

where both equations implicitly define  $k_3 = k_3(k_1, k_2)$ .  $k_4$  is obtained from momentum conservation as  $k_4 = k_1 + k_2 - k_3 \bmod 1$ , resp.  $k_4 = k_1 + k_2 + k_3 \bmod 1$ . Mostly one has to work with this implicit definition and only in very exceptional cases an explicit collision formula is available. An instructive example is the case one space dimension. Mechanical particles would merely exchange labels and the Boltzmann collision operator vanishes. On the other hand, for phonons in one dimension with an  $\omega$  derived from nearest neighbor couplings, (3.2) has a nondegenerate solution, thus providing real phonon collisions [27], [28]. In principle, it may happen that the energy-momentum conservation laws have no solution at all. Then the collision term vanishes. In case of several solutions one has to sum over all of them. Note that in (2.4) energy conservation cannot be satisfied for the term with  $\sigma_j = 1$ ,  $j = 1, 2, 3$ . This term had

been added only to have a more symmetric looking expression. A further instructive example are nearest neighbor couplings, for which the dispersion relation reads

$$\omega(k) = \left( \omega_0^2 + 2 \sum_{j=1}^3 (1 - \cos(2\pi k^j)) \right)^{1/2}, \quad k = (k^1, k^2, k^3) \in \mathbb{T}^3. \quad (3.4)$$

Then (3.3) has no solution and collision processes where three phonons merge into one, and their time reversal, are forbidden. As for dilute gases, there are only number conserving pair collisions. Such a property is stable under small perturbations of  $\omega$ . It also holds for the nonlinear wave equation (1.1) for which  $\omega(k) = |k|$ ,  $k \in \mathbb{R}^3$ .

The equilibrium measure for the harmonic part is the Gaussian  $Z^{-1} \exp[-\beta H_{\text{har}}]$  with  $Z$  the normalizing partition function and  $\beta$  the inverse temperature,  $\beta > 0$ . The anharmonic potential can be neglected in the kinetic limit. The corresponding Wigner function,  $W_\beta$ , is given by

$$W_\beta(k) = \frac{1}{\beta \omega(k)}, \quad (3.5)$$

in the limit of an infinitely extended lattice, compare with (1.16). Using (2.4), it follows that

$$\begin{aligned} \mathcal{C}(W_\beta)(k) &= (3.6) \\ &= \frac{3\pi}{4} \sum_{\sigma_1, \sigma_2, \sigma_3 = \pm 1} \int_{\mathbb{T}^3} dk_1 dk_2 dk_3 (\omega \omega_1 \omega_2 \omega_3)^{-1} \delta(\omega + \sigma_1 \omega_1 + \sigma_2 \omega_2 + \sigma_3 \omega_3) \\ &\quad \times \delta(k + \sigma_1 k_1 + \sigma_2 k_2 + \sigma_3 k_3) \beta^{-3} (\omega \omega_1 \omega_2 \omega_3)^{-1} (\omega + \sigma_1 \omega_1 + \sigma_2 \omega_2 + \sigma_3 \omega_3) \\ &= 0, \end{aligned}$$

as expected. The issue whether there are further stationary solutions will be discussed below.

Following Boltzmann, to define the entropy one first has to identify a family of macroscopic observables. If for simplicity, and in fact for the remainder of this section, we restrict ourselves to the spatially homogeneous situation, then in spirit the macrovariables are the phonon numbers  $a(k)^* a(k)$ ,  $k \in \mathbb{T}^3$ . To be more precise one has to employ the limit procedure of Boltzmann, the only difference being that here we have to take into account the harmonic couplings. We partition the torus  $\mathbb{T}^3$  into cubes  $\Delta_j$  of side length  $\delta$ ,  $j = 1, \dots, M^3$ ,  $\delta M = 1$ . We consider a finite lattice volume,  $\ell^3$ , which is equivalent to discretizing the torus  $\mathbb{T}^3$  to  $(\mathbb{T}_\ell)^3$  with grid spacing  $\ell^{-1}$ . The proper macrovariables are then

$$H_j = \sum_{k \in \Delta_j \cap (\mathbb{T}_\ell)^3} a(k)^* a(k), \quad j = 1, \dots, M^3. \quad (3.7)$$

For a given Wigner function  $W$  the cell in phase space at precision  $\ell^3 \varepsilon$  is defined by the conditions

$$\{(q, p) \in (\mathbb{R}^2)^{\ell^3} \mid \ell^3(e_j - \varepsilon) \leq H_j(q, p) \leq \ell^3(e_j + \varepsilon), \quad j = 1, \dots, M^3\} \quad (3.8)$$

with

$$e_j = \delta^3 \int_{\Delta_j} dk W(k). \quad (3.9)$$

The entropy  $S(W)$  of  $W$  is defined as  $\ell^{-3}$  times the logarithm of the Lebesgue measure of the set in (3.8) upon taking limits in the following order:  $\ell \rightarrow \infty$ ,  $\varepsilon \rightarrow 0$ ,  $\delta \rightarrow 0$ . The net result is

$$S(W) = \int_{\mathbb{T}^3} dk \log W(k), \quad (3.10)$$

up to a constant independent of  $W$ .

Before computing the rate of change of the entropy let us introduce the notion of a collisional invariant. This is a function  $\psi: \mathbb{T}^3 \rightarrow \mathbb{R}$  which satisfies either one of the following functional equations.

(i) *Pair collisions:*

$$\psi(k_1) + \psi(k_2) = \psi(k_3) + \psi(k_1 + k_2 - k_3) \quad (3.11)$$

on the set  $\{(k_1, k_2, k_3) \in \mathbb{T}^9 \mid \omega(k_1) + \omega(k_2) = \omega(k_3) + \omega(k_1 + k_2 - k_3)\}$ .

(ii) *Three phonons merger:*

$$\psi(k_1) + \psi(k_2) + \psi(k_3) = \psi(k_1 + k_2 + k_3) \quad (3.12)$$

on the set  $\{(k_1, k_2, k_3) \in \mathbb{T}^3 \mid \omega(k_1) + \omega(k_2) + \omega(k_3) = \omega(k_1 + k_2 + k_3)\}$ .

If  $W$  evolves according the spatially homogeneous kinetic equation (2.3), then

$$\begin{aligned} \frac{d}{dt} S(W) &= \int_{\mathbb{T}} dk_1 W(k_1)^{-1} \mathcal{C}(W)(k_1) \\ &= 12\pi \sum_{\sigma_1, \dots, \sigma_4 = \pm 1} \int_{\mathbb{T}^4} dk_1 dk_2 dk_3 dk_4 (16\omega_1\omega_2\omega_3\omega_4)^{-1} \delta\left(\sum_{j=1}^4 \sigma_j \omega_j\right) \delta\left(\sum_{j=1}^4 \sigma_j k_j\right) \\ &\quad \times W_1^{-1} \sigma_1 (\sigma_1 W_2 W_3 W_4 + W_1 \sigma_2 W_3 W_4 + W_1 W_2 \sigma_3 W_4 + W_1 W_2 W_3 \sigma_4) \\ &= 3\pi \sum_{\sigma_1, \dots, \sigma_4 = \pm 1} \int_{\mathbb{T}^4} dk_1 dk_2 dk_3 dk_4 (16\omega_1\omega_2\omega_3\omega_4)^{-1} \delta\left(\sum_{j=1}^4 \sigma_j \omega_j\right) \delta\left(\sum_{j=1}^4 \sigma_j k_j\right) \\ &\quad \times W_1 W_2 W_3 W_4 \left(\sum_{j=1}^4 \sigma_j W_j^{-1}\right)^2. \end{aligned} \quad (3.13)$$

We conclude that the entropy production is non-negative and that  $dS(W)/dt = 0$  if and only if  $1/W$  is a positive collisional invariant.

Vice versa, if  $\psi$  is a collisional invariant and  $\psi(k) \geq 0$ , then setting  $W(k) = 1/\psi(k)$  one has

$$\mathcal{C}(W)(k) = 0. \quad (3.14)$$

Thus stationary solutions are uniquely characterized by  $1/W$  being a positive collisional invariant. In brackets we remark that a complete discussion would have to specify in which function space one searches for collisional invariants.

Collisional invariants are studied in [29], where the following result is proved.  $\omega$  is assumed to have no flat pieces in the sense that the set  $\{k \in \mathbb{T}^3 \mid \det \text{Hess } \omega(k) = 0\}$  has at most the dimension two. Here Hess is the Hessian of  $\omega$  as a  $3 \times 3$  matrix. Let  $\psi : \mathbb{T}^3 \rightarrow \mathbb{R}$  be measurable,  $\int_{\mathbb{T}^3} dk |\psi(k)| < \infty$ , and a collisional invariant under pair collisions, in the sense that (3.11) holds Lebesgue almost surely. Then  $\psi$  is necessarily of the form

$$\psi(k) = a + c\omega(k) \quad (3.15)$$

with some constants  $a, c \in \mathbb{R}$ . By our previous discussion this implies that the kinetic equation has a two-parameter family of stationary solutions. If (3.15) is inserted in the 3-phonons merger (3.12), then  $a = 0$  necessarily. To have thermal equilibrium as only stationary solutions, there must be 3-phonons mergers on a set of full dimension. A more physical mechanism would be to include a cubic on-site potential, which appears naturally in an expansion with respect to the anharmonicity, unless there are special symmetries which would make this order to vanish. For the cubic potential a collisional invariant must satisfy the 2-phonons merger condition, which is (3.12) upon dropping  $k_3$ . Again, if there is a set of full dimension of 2-phonons mergers, then the only stationary solutions are the ones corresponding to thermal equilibrium.

Our discussion has interesting implications on the very widely studied Fermi–Pasta–Ulam problem [30], see the special issue [31] at the occasion of its 50-th anniversary. Fermi, Pasta, and Ulam considered chains of anharmonic oscillators and studied by a numerical iteration scheme the relaxation to equipartition, i.e. to thermal equilibrium. To their surprise, such an approach did not take place, at least not on the time scale of the computation. One explanation comes from the KAM theory which demonstrates that in part the invariant tori of the linear dynamics persist under small nonlinear perturbations. Thus a Lebesgue typical phase point may not explore the full energy shell. A second explanation relies on the fact that for a special choice of the nonlinearity the Hamiltonian system remains integrable and admits propagating soliton solutions. Also, for the FPU model there are special solutions, the breathers, which may impede the relaxation to thermal equilibrium.

Kinetic theory operates in a different part of phase space. The energy is proportional to the length of the chain and the nonlinearity is weak. In this regime the phonon picture is precise. Propagation is encoded by the dispersion relation  $\omega$ , while the relaxation comes from the phonon collisions. For the FPU chain one has  $\omega(k) = (1 - \cos(2\pi k))^{1/2}$ ,  $k \in \mathbb{T}$ . Thus, ignoring special  $k$ -values, phonons propagate ballistically with non-zero speed. On the other hand, the collision rule depends on the precise form of the nonlinearity. For the FPU  $\alpha$ -chain the couplings are cubic as  $(q_{j+1} - q_j)^3$ . In this case the collision term vanishes which signals poor relaxation. For the FPU  $\beta$ -chain the couplings are quartic as  $(q_{j+1} - q_j)^4$ . A detailed analysis shows that the energy current correlation, as based on kinetic theory, has a slow decay as  $t^{-3/5}$  [27], [33], a result with good numerical support [32]. If instead one chooses as nonlinearity a quartic on-site potential, as  $q_j^4$ , then the energy current correlation decays exponentially [28]. In this case kinetic theory predicts a rapid convergence to equilibrium, as is well confirmed by molecular dynamics simulations [28], [34], also away from the limiting kinetic regime.

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*Reise eines deutschen Professors ins Eldorado*  
Drawing by Karl Przibram  
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# Entropy, probability and dynamics

E. G. D. Cohen

## Introduction

Boltzmann had a strong disposition for mechanics and his first papers were all devoted to purely mechanical derivations of the Second Law of Thermodynamics. The most important one was that based on the 1872 Boltzmann equation, i.e. on the dynamics of binary collisions, where he says at the end:

*“One has therefore rigorously proved that, whatever the distribution of the kinetic energy at the initial time might have been, it will, after a very long time, always necessarily approach that found by Maxwell”* [1].

He seems to have overlooked entirely that the Stoßzahlansatz, i.e. the assumption of molecular chaos used in his equation, was a statistical assumption which had no dynamical basis.

It is therefore, in my opinion, ironic that perhaps his most famous achievement may well have been the relation of 1877 between entropy and probability, which was devoid of any dynamical feature [2].

Whenever later dynamical results were obtained, e.g. by Helmholtz, when he introduced his monocycles in 1884 [3], Boltzmann immediately jumped at it and extended it to what we now call the origins of ergodic theory, i.e. a dynamical theory [4]. Also his summarizing lectures in the two volume “Lectures on Gas Theory” [5] mostly discuss dynamical approaches and e.g. reference to the entropy-probability relation can mainly be found on a few pages of the first book in connection with the statistical interpretation of his  $H$ -function ([5], I, p. 38–42).

However, in this lecture I do want to concentrate on his work on entropy and probability first and end with a revival of the dynamical approach as proposed by Einstein and as later used, in my view, in the dynamical approach to phase space probabilities in the Sinai–Ruelle–Bowen (SRB) distribution. The sudden switch which Boltzmann made from a purely dynamical to a purely probabilistic approach, might well have been due to the critical attacks of many of his colleagues on the Stoßzahlansatz, as exemplified by Loschmidt’s Reversibility Paradox [6] and Zermelo’s Recurrence Paradox [7].

## 1 Boltzmann’s original derivation of $S \sim \log W$

This was done in a paper of 1887<sup>[2]</sup>: *“On the relation between the Second Law of the Mechanical Theory of Heat and Probability Theory with respect to the laws of thermal equilibrium.”* I will sketch first the simplified procedure Boltzmann follows in Chapter I of this paper.

The crucial statement here is: "For an ideal gas in thermal equilibrium the probability of the number of "complexions" of the system is a maximum."

Boltzmann introduced the notion of "complexions" as follows:

a) Assume discrete kinetic energy values of each molecule, which are represented in an arithmetic series:

$$\varepsilon, 2\varepsilon, 3\varepsilon, \dots, p\varepsilon,$$

where each molecule can only have a finite number,  $p$ , of kinetic energies  $\varepsilon$ .

b) Before each binary collision the total kinetic energy of the two colliding molecules is always contained in the above series and "by whatever cause" the same is true after the collision. He says:

*"There is no real mechanical system [to which this collision assumption is applicable], but the so-defined problem is mathematically much easier to deal with and [in addition] it goes over in the problem we want to solve, when the kinetic energies of the molecules become continuous and  $p \rightarrow \infty$ ".*

Assume that the possible kinetic energies of the  $N$  molecules are distributed in all possible ways at constant total kinetic energy  $E$ . Then each such distribution of the total kinetic energy over the molecules is called a *complexion*. What is the number  $P$  of complexions, where  $w_j$  molecules possess a kinetic energy  $j\varepsilon$  ( $j = 1, \dots, N$ )? This number  $P$  [which Boltzmann calls "the permutability" or "thermodynamic probability"] indicates how many complexions correspond to a given molecular distribution or state of the system. A distribution can be represented by writing down first as many  $j$ 's as there are molecules with a kinetic energy  $j\varepsilon$  ( $w_j$ ) etc. Obviously  $P = N! / \prod_{j=1}^p w_j!$ . The most probable distribution is that for which the  $\{w_j\}$  are such that  $P = \max$  or  $\prod_{j=1}^p w_j!$  or also  $\log \prod_{j=1}^p w_j!$  a minimum. With the constraints  $\sum_{j=1}^p w_j = N$  and  $\sum_{j=1}^p (j\varepsilon) w_j = E$  and Stirling's approximation, Boltzmann finds then for the probability that the kinetic energy of a molecule is  $s\varepsilon$ :

$$w_s \sim \exp -s\varepsilon/\bar{\varepsilon}$$

with  $\bar{\varepsilon} = \frac{E}{N}$ , the average kinetic energy of a molecule.

Boltzmann adds that: "*in order to translate the above [derivation] into the mechanical theory of heat, in particular into the introduction of differentials [when one makes the kinetic energies of the molecules continuous rather than discrete], needs still some thought and a not unimportant modification of the formulae.*"

This was worked out in the following three chapters of this paper.

It ultimately leads then to the results that  $\max P$  yields Maxwell's exponential kinetic energy distribution as well as to the developments in Chapter V, which I will now discuss.

In Chapter V of this paper Boltzmann discusses the "*Relation of the Entropy to that quantity, which I have called the [thermodynamic] probability distribution*". He first makes the connection between what he calls the *degree of permutability*  $\Omega$  or  $\log P$  given by:

$$\Omega = - \iint f(\mathbf{r}, \mathbf{v}) \log f(\mathbf{r}, \mathbf{v}) d\mathbf{r} d\mathbf{v}$$

and the entropy. Here  $f(\mathbf{r}, \mathbf{v})$  is a continuous generalization of the discrete  $w_j$  used before, giving the number of molecules at the position  $\mathbf{r}$  with velocity  $\mathbf{v}$ . The maximum of  $\Omega$  under the constraints that  $N$  and  $E$  are given, leads then again to the exponential Maxwell equilibrium velocity distribution. Noting that the degree of permutability  $\Omega$  differs from the logarithm of the permutability  $P$  by a constant, one has  $\Omega = \log P + \text{constant}$ . If the gas was initially not in thermal equilibrium and approaches equilibrium,  $\Omega$  must reach a maximum  $\Omega_{\max}$ . Boltzmann then computes *thermodynamically* the entropy  $S$  for an ideal gas with  $N$  particles and average kinetic energy or temperature  $T$ . For reversible processes he finds then:

$$S = \int dQ/T = \Omega = \log P + \text{constant}.$$

As Abraham Pais remarks in his classic book “Subtle is the Lord....” [8]: “*Boltzmann’s qualities as an outstanding lecturer are not reflected in his scientific papers, which are sometimes unduly long, occasionally obscure and often dense. Their main conclusions are sometimes tucked away among lengthy calculations.*”

The paper I am discussing is a prime example of this description. Only in the text towards the end of the paper the following sentence appears referring to the previously obtained formula  $S = \int dQ/T = \Omega$  when he says:

“Now it is known that when in a system of bodies only **reversible** changes occur, the total entropy of all these bodies remains constant. If, however, also **irreversible** processes occur, then the total entropy of the system must necessarily grow....”

According to the equation

$$d\Omega = d \log P = dQ/T = dS$$

the increase in the degree of permutability of a system  $d\Omega$  equals then the increase of its entropy  $dS$ . He says:

“Therefore the degree of permutability  $\Omega$  is a quantity, which in the equilibrium state, apart from a constant factor and an addend, is identical with the entropy  $S$ .”

That is:  $S = c_1\Omega + c'_2 = c_1 \log P + c_2$ , but this formula is *not* in the paper.

Boltzmann ends this very long [60 pages] paper by remarking that too little is known both experimentally and theoretically about liquids and solids, to generalize his relation  $S = c_1 \log P + c_2$  from ideal gases to liquids or solids. He remarks that he “*has given earlier arguments that it is likely that also for these states of aggregation, thermal equilibrium will be determined by a maximum of the quantity  $\Omega$ , which [also] for such systems [would be] identical with the entropy  $S$ .*”

## 2 Planck’s derivation of Boltzmann’s $S = c_1 \log P + c_2$

It was really Planck who made the step from Boltzmann’s paper to  $S = k \ln W + c$ , where  $W$  is written instead of  $P$  [9]. Planck bases his discussion of the connection between entropy and probability on the universality of both the Second Law and the

laws of probability, “so that it is to be expected that the connection between entropy and probability should be very close”.

Hence he makes the following proposition as the foundation of all further discussion: “*The entropy of a physical system in a definite state depends solely on the [thermodynamic] probability  $W$  [ $\equiv P$ ] of this state.*”

Without knowing this probability  $W$ ,  $S$  can be determined as follows.

**Planck's derivation of Boltzmann's  $S = f(W)$ .** The probability  $W$ , for a system consisting of two entirely independent systems with probabilities  $W_1$  and  $W_2$ , respectively, is:  $W = W_1 W_2$ . Then  $S_1 = f(W_1)$  and  $S_2 = f(W_2)$ . Second Law:  $S = S_1 + S_2$  or  $f(W_1 W_2) = f(W) = f(W_1) + f(W_2)$ . Differentiating both sides of this equation with respect to  $W_1$  with  $W_2 = \text{constant}$  and then the resulting equation with respect to  $W_2$  at  $W_1 = \text{constant}$  one obtains

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

with the solution  $f(W) = k \log W + \text{constant}$  or  $S = k \log W + c$ . Thus Planck formulated Boltzmann's connection between entropy  $S$  and the permutability  $P \sim W$ , in its definitive form:

$$S = k \log W.$$

Planck notices two differences between his formula and Boltzmann's expression  $S = c_1 \log P + c_2$ :

a) He replaces Boltzmann's macroscopic expression for  $c_1 = R/N$  by a molecular quantity which he called Boltzmann's constant  $k$ .

b) The additive constant  $c_2$  is undetermined as is the case in the whole of classical thermodynamics. Planck assigns a definite value to  $c_2$ , i.e. a definite value to  $S$ , by using the “hypothesis of quanta”.

That is, he assumed that in every finite region of phase space the thermodynamic probability has a finite magnitude limited by [the existence of]  $h$ , Planck's constant, and can not be infinitesimally small like in the classical case. This allows  $S$  to be determined free of an arbitrary constant  $c_2 = 0$  and at the same time to connect the classical and quantum mechanical values of  $S$ , such that  $S = 0$  at  $T = 0$  (Sackur-Tetrode formula) [10].

To the best of my knowledge neither Boltzmann's nor Planck's derivation of  $S$  for an ideal gas has ever been generalized to an interacting gas. Results for such a gas can be obtained from Gibbs' microcanonical ensemble but that is based ultimately on the unproven ergodic hypothesis.

### 3 Einstein's objection

1. From 1905–1920 Einstein repeatedly objected to the probabilistic derivation of  $S = k \log W$  [11], [13], [12].

2. Basis: the thermodynamic probability  $W$  to find the system in a certain complex-ion can *only* be determined *dynamically* and not be guessed statistically by assigning “ad hoc permutabilities” ( $P$ ) to complexions of the system.

3. In fact, it is determined by the frequency that a phase space trajectory visits a given region of phase space due to its *dynamics* in phase space.

**Quote of 1910 [13].** “*Usually  $W$  equals the number of complexions. In order to compute  $W$  [however] one needs a **complete** (molecular-mechanical) theory of the system. Therefore it is dubious that the Boltzmann principle has any meaning **without** a **complete** molecular-mechanical theory or some other theory which describes the elementary [dynamical] processes [of the system]. In equilibrium, the expression  $S = k \log W + c$ , seems [therefore] devoid of [any] content from a phenomenological point of view, without giving in addition such an elementary theory.*”

## 4 The SRB distribution

Recently a theory has been developed for systems in a *non-equilibrium* stationary state, which are in principle, not restricted to be near equilibrium. This theory uses a probability or measure for “complexions” of the system in its phase space following Einstein’s dynamical rather than Boltzmann’s (probabilistic) Principle, as Einstein called it. This measure is usually called the Sinai–Ruelle–Bowen or SRB measure, see e.g. [14], which will be sketched in a physical way now. For simplicity, I will use a two dimensional representation.

Consider a smooth and very chaotic classical dynamical system (Anosov-like) evolving in discrete time via a map of phase space. This chaoticity is based on the hyperbolicity of the points representing the system in its phase space. Each such point has two manifolds (cf. Figure 1):

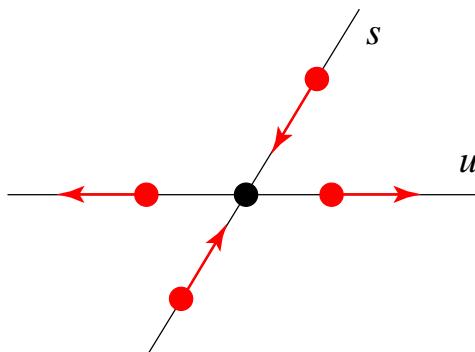


Figure 1. Unstable ( $u$ ) and stable ( $s$ ) manifolds associated with a phase point (thick bullet) in a two dimensional representation.

a) an *unstable* manifold ( $u$ ), on which two separate points near a given phase point exponentially *separate* from each other;

b) a *stable* manifold ( $s$ ) on which two separated points near a given phase point exponentially *approach* each other.

Then one makes a special partition of the phase space into “parallelograms” (cells, cf. Figure 2): the “horizontal sides” of which consist of unstable manifolds, while their “vertical” sides consist of stable manifolds. The partition is special in the sense that it is a “Markov partition”, i.e. a partition into parallelograms such that the union of their stable boundaries is shrunk into itself, while for the inverse map the same happens for the unstable boundaries [21].

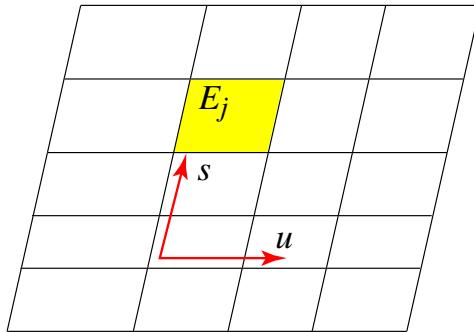


Figure 2. Markov partition of a two dimensional phase space with cells  $E_j$ , formed by the unstable ( $u$ ) and stable ( $s$ ) manifolds of the phase points.

The size of these parallelograms is determined by a parameter  $\mathcal{T}$ , so that for  $\mathcal{T} \rightarrow \infty$  their sizes go to zero. Now each cell  $E_j$  in phase space is given a weight  $\Lambda_{u,\tau}^{-1}(x_j)$  which is equal to the inverse of the phase space expansion along the unstable manifold, during a time  $\tau$ . This phase space expansion is based on a trajectory moving during a (discrete) time  $\tau$  from  $-\tau/2 - 1$  to  $\tau/2$  along a phase space trajectory through the center  $x_j$  of the cell  $E_j$ , using the dynamical equations of motion (cf. Figure 3).

Considering a small phase space volume  $A$  around the initial point at  $-\tau/2 - 1$  (cf. Figure 4), then all points in  $A$  will go via phase space trajectories to corresponding points in the phase space volume  $B$  around the final point at  $+\tau/2$ . The larger the phase space volume expansion  $\Lambda_{u,\tau}(x_j)$  in the direction of the unstable manifold  $u$  is, i.e. the larger  $L_B/L_A$ , the more the phase space trajectories will tend to avoid (bypass) the point  $x_j$ .

The inverse of this ratio  $\sim L_A/L_B \sim \Lambda_{u,\tau}^{-1}(x_j)$  will therefore be a measure of the “eagerness” or frequency of the phase space trajectories to be near  $x_j$ , i.e. that the system will visit the cell  $E_j$ . Weighing the Markov partitions in phase space this way, one obtains in a *dynamical* way the probability to find the system anywhere in phase space. As a consequence, the average of a smooth function  $F(x)$ , where  $x$  denotes a

point in phase space, is then determined by the SRB measure  $\Lambda_{\tau,u}^{-1}(x_j)$ :

$$\int \mu_{SRB}(dx) F(x) = \lim_{\tau \geq \tau/2 \rightarrow \infty} \frac{\sum_j \Lambda_{u,\tau}^{-1}(x_j) F(x_j)}{\sum_j \Lambda_{u,\tau}^{-1}(x_j)}$$

This appears to me a direct example of Einstein's proposal of a probability for complexions based on the system's *dynamics* rather than on ad hoc, although possibly reasonable, probabilistic assumptions as made by Boltzmann and Planck.

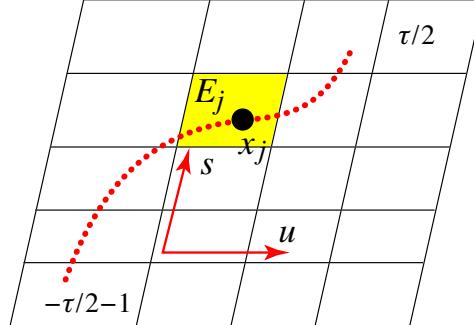


Figure 3. Trajectory segment of duration  $\tau$  through the center  $x_j$  of cell  $E_j$  of a Markov partition of the system in phase space.

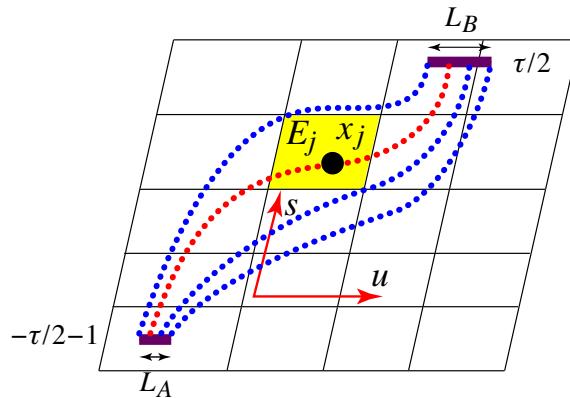


Figure 4. Small phase space volume of extension  $L_A$  at time  $-\tau/2 - 1$  and of extension  $L_B$ , in the direction of the unstable manifold ( $u$ ) at time  $\tau/2$ .  $L_B/L_A$  gives the phase space volume increase in the direction of the unstable manifold ( $u$ ).

## 5 Final remarks

1. In thermal equilibrium the SRB distribution reduces to Gibbs' microcanonical ensemble. This implies that this ensemble can also be derived rigorously dynamically along the lines sketched here, albeit so far only for smooth and sufficiently chaotic systems. The role of coarse graining phase space into physically infinitesimal cells, to go from a microscopic to a macroscopic description, which is used in various ways in all classical derivations of thermodynamics from statistical mechanics and also by Boltzmann and Planck, is only used in passing in the SRB measure, because of the ultimate  $\lim_{\tau \geq \tau/2 \rightarrow \infty}$ .

2. To actually use Einstein's dynamical method to determine the probabilities of cells in phase space in practice, requires a solution of the equations of motion. The only way, so far, around this fundamental difficulty has been to replace the effects of dynamics again by suitable probability distributions as is done e.g. in superstatistics [15], [16], [17]. This has been applied successfully to certain distribution functions in turbulent flows by using e.g. log-normal or  $\chi^2$ -distributions.

3. To the best of my knowledge there is no definition of entropy beyond the linear (near equilibrium) regime. This is in my opinion a fundamental open question, whose solution may be essential to make real progress into the far from equilibrium region. Gallavotti and I [18] have conjectured that the entropy in nonequilibrium stationary states "far" from equilibrium cannot be defined, just like the heat content of a body in equilibrium cannot be defined, since it depends on how this heat is used [19]. Similarly, entropy *differences* such as entropy production or entropy transfers could be meaningful also far from equilibrium, just like heat production or heat transfer are in equilibrium.

4. In all fairness to Boltzmann, it should be said that he also proposed to determine the probability of a state or a complexion of a system in a region of phase space of this system in equilibrium, by assuming that this probability would be proportional to the *time* the system spends in it i.e. involving the dynamics of the system. But for some reason he did not develop this idea further.

Finally it would be, in my opinion, a grave mistake to think that Boltzmann would have been opposed to these new dynamical developments. As I said before, he had a strong disposition for dynamics and I think his probabilistic work was presumably inspired to get rid of his many opponents to his dynamical work and was just an intermezzo for him, important as it is for us.

In fact, Boltzmann would have been delighted to see that a dynamical theory of phase space weights was developed and used a century after his death and that therefore his dynamical predilection was justified in the end, compatible with Einstein's objection [20].

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# Realizing Boltzmann's dream: computer simulations in modern statistical mechanics

Christoph Dellago and Harald A. Posch

## 1 What if?

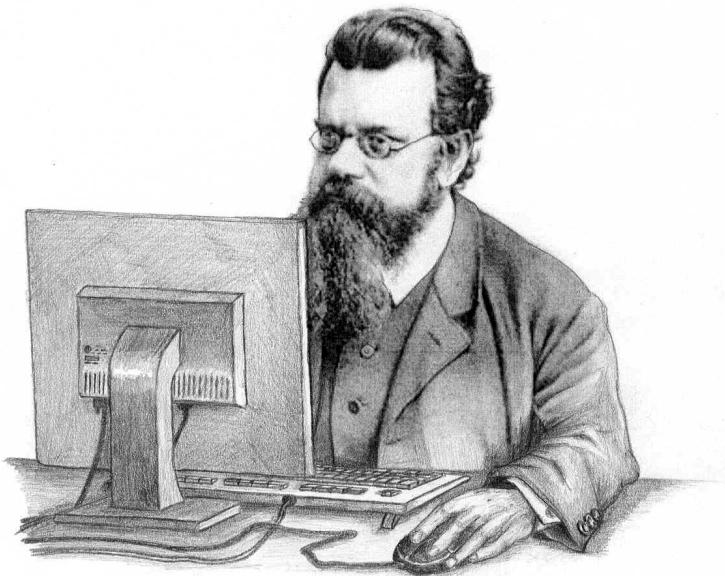


Figure 1. Boltzmann at work (Drawing by Bernhard Reischl, University of Vienna).

What would Boltzmann have done with a computer? Of course, any answer to this question is highly speculative, but it is easy to imagine that Boltzmann would have realized what a wonderful tool for scientific research and discovery the computer is, particularly in his field of statistical mechanics. Most likely, Boltzmann would have invented the molecular dynamics method and used it to test and further develop the molecular models of matter he and his contemporaries created. All he required he already knew, and his motivation is more than clear from his work. With such simulations, Boltzmann literally could have watched how a system relaxes towards equilibrium, and he could have performed a numerical analysis of the validity of the assumption of molecular chaos, which is so central to his kinetic equation. Certainly, he would have determined the equations of state of dilute gases and of dense liquids and solids. One may further speculate that Boltzmann would have made creative use of modern visualization tools

that, today, are of such crucial importance in simulation studies and provide insight and guidance not available otherwise. It is also amusing to think about what Boltzmann would *not* have done, if he had had access to a computer. For instance, would Boltzmann have bothered to write down the Boltzmann equation? Perhaps he would just have run a molecular dynamics simulation for hard spheres with simple collision rules to follow the dynamics of his model gas. From such a simulation he could have calculated properties of dilute and dense gases in order to compare them with experimental data. Then, the need to write down an approximate and complicated integro-differential equation that cannot even be solved analytically except for very simple cases would not have arisen. Or would Boltzmann have tried to develop a virial expansion for the hard sphere gas if he could have determined the equation of state with high precision from simulations? Nobody knows, but statistical mechanics might have unfolded in a completely different way, if computers had been available at Boltzmann's time. While it is not hard to imagine where Boltzmann would have begun his computational investigation, it is impossible to predict where insights gleaned from simulations would have taken a mind like his.

In this article we will take a more modest attitude and reflect on the significance of computer simulations in the research program initiated by Boltzmann and his contemporaries. Since the advent of fast computing machines in the 1940s and 1950s, computer simulations have played an increasingly important role in statistical mechanics and have provided the field with an enormous boost. The main reason for this success story is that complex correlations make most interesting systems intractable with analytical tools. In equilibrium statistical mechanics, for instance, only very few models have been solved analytically so far. Examples include the ideal gas, the harmonic solid, and, perhaps most famously, the two-dimensional Ising model, which was solved by Onsager in a mathematical *tour de force*. In essence, analytical solutions can be achieved only in the absence of correlations either because the model does not exhibit any (such as the ideal gas or the harmonic solid) or because approximations are used, in which correlations are neglected to a certain degree as is done in mean field theories such as the molecular field theory of magnetism and the van der Waals theory. When correlations become important, however, these theories fail. There are, of course, exceptions such as the 2d-Ising model, but in this case the exact analytical solution is possible only by very specific mathematical tricks which are not helpful for illuminating the underlying physics. In non-equilibrium statistical mechanics the situation is even worse and almost nothing is known analytically. In computer simulations, on the other hand, correlations can be fully treated, and also non-equilibrium systems can be studied essentially without the need of uncontrolled approximations. Therefore, it is not surprising that computer simulations have grown into one of the most important and powerful theoretical tools in statistical mechanics and, particularly, the physics of condensed matter. Interestingly, the rapid progress in computer simulation is only partially due to the fast growth in raw computing power, which, according to Moore's law, doubles every 18 months. The more important factor turns out to be the development of better simulation algorithms. For instance, it has been estimated that between 1970 and 1995 computing power increased by a factor of  $10^4$ , while the total

computing speed in the simulation of spin models grew by a factor of  $10^{10}$  [1].

In the context of Boltzmann's science and legacy, computer simulations play a multifaceted role:

- Computer simulations are used to carry on Boltzmann's program to establish the properties of macroscopic matter from a knowledge of the microscopic constituents. Today, statistical mechanical computer algorithms, such as Monte Carlo and molecular dynamics simulations, are routinely used, often with energies and forces obtained from first-principles electronic structure calculations, to study the properties of complex molecular aggregates ranging from materials to biological systems.
- Boltzmann's ideas and results have been confirmed by computer simulations. For instance, Boltzmann's  $H$ -theorem was numerically examined for a system of hard disks and was found to hold except for small fluctuations during which  $H(t)$  briefly increased manifesting the statistical character of the Second Law of Thermodynamics [2].
- Computer simulations interact with analytical theory by testing the assumptions that are made in order to obtain mathematically treatable expressions. For instance, the hypothesis of molecular chaos on which the Boltzmann equation relies, can be directly tested using molecular dynamics simulations. Such calculations can also guide the development of better approximations.
- Computer simulations have not only helped to solve equations that are too complicated to be solved analytically such as Newton's equations of motion, but have also provided the impetus for the development of new theoretical approaches. In particular, the search for better simulation algorithms has motivated, driven and guided the advancement of statistical mechanical theories particularly in the field of non-equilibrium processes. For instance, Jarzynski's non-equilibrium work theorem discussed in Section 6 arose out of efforts to develop efficient methods for the calculation of equilibrium free energies. These new fundamental developments are in turn used to derive more efficient computational algorithms [3], [4], [5].
- Computer simulations promote physical understanding by illustrating fundamental concepts for simple models that can be thoroughly simulated and visualized. As an example we mention the Lorentz gas, which in Section 3 is used to illustrate mixing in phase space, and in Section 7 to discuss systems far from thermodynamic equilibrium.
- Boltzmann's ideas and results provide the theoretical foundation for modern computer simulation algorithms. For example, equilibrium statistical mechanics as developed by Boltzmann and Gibbs is the basis for Monte Carlo simulations in various ensembles.

In the following sections we will discuss some of these points in more detail and illustrate how computer simulations have helped to improve our understanding of statistical mechanical systems in general, and of Boltzmann's ideas in particular. The choice of examples is, naturally, biased towards our own main scientific interests which are in the fields of molecular simulation, non-linear dynamics and non-equilibrium statistical mechanics.

It has been often remarked that no real understanding can be obtained from computer simulations. Now, it is certainly true that a detailed molecular dynamics trajectory, stored in a computer file in the form of a time series of the positions and momenta of all particles for consecutive time steps, by itself does not generate understanding of the simulated system. But the same can be said for analytical results. What, for instance, do we learn from a detailed wave function available analytically for a large many particle system? Or what do we gain from the partition functions of equilibrium statistical mechanics that are, in principle, always available analytically, albeit as complicated integrals that can only rarely be solved in a closed form? In all these cases, only further analysis yields useful information and helps to identify the variables that capture the relevant physics and separate them from irrelevant degrees of freedom that may be treated as random noise. Similarly, only further data analysis, carried out analytically or numerically, helps to extract the meaningful information from simulations, which makes true understanding possible.

## 2 Atoms exist

One of the main scientific objectives of Boltzmann and contemporaries such as Clausius, Maxwell, and van der Waals was to prove that matter consists of atoms, little particles interacting with each other and moving according to the rules of Newtonian mechanics. The method they chose to carry out this ambitious program was to postulate that atoms exist and to deduce empirically testable consequences from this hypothesis. Since in Boltzmann's days experimental techniques to probe the microscopic properties of matter were not available, the only way to verify the atomic hypothesis was to derive macroscopic observables such as the equation of state, the viscosity, or the heat conductivity of a gas from the postulated atomic constituents of matter.

As emphasized by Laplace, a system of particles evolving in time according to the laws of Newtonian mechanics is completely deterministic. So, in principle, the properties of, say, a gas can be determined by solving the equations of motion for all particles starting from suitably chosen initial conditions. Naturally, to do so with the theoretical tools available to Boltzmann and his contemporaries was out of the question. However, Clausius, Maxwell and Boltzmann realized that no detailed information on the positions and velocities of all the particles is required for predicting the macroscopic properties of many-particle systems. Rather, it is sufficient to consider probability densities that describe the system only in a statistical sense. This approach, referred to as kinetic theory, turned out to be highly successful and provided the basis for the Boltzmann equation and the statistical interpretation of irreversibility. But also in this

probabilistic framework, the computation of macroscopic properties remains highly non-trivial in most circumstances. Essentially, the fundamental equations of kinetic theory can be analytically solved only if correlations may be neglected to a certain degree, as is the case for dilute gases. (For a historic overview of kinetic theory we refer the reader to [6]).

This situation remained essentially unchanged until fast computing machines became available and the molecular dynamics simulation method was invented in the 1950s. In this computational approach, the basic idea is to follow the time evolution of a particle system in full detail by solving Newton's equations of motion in small time steps. By iterating this procedure many times, one may obtain an approximation to the dynamical trajectory of the system in phase space and extract structural as well as dynamical information such as time correlation functions from it. A molecular dynamics simulation generates the full dynamical information including complex correlations that are usually neglected in analytical treatments. For a realistic description of real systems, an accurate calculation of the forces acting between the particles is of course crucial. While early simulations of liquids and solids used simple interaction potentials such as the Lennard-Jones potential or the hard sphere potential, sophisticated empirical force fields now exist for a variety of systems ranging from simple and complex fluids to assorted materials and biological macromolecules. Using these methods on modern computers, one can simulate equilibrium as well as non-equilibrium systems consisting of millions of atoms on the nanosecond time scale and determine their microscopic and macroscopic properties. Methods are now also available to calculate from first principles effective interatomic potentials mediated by electrons. Based mainly on density functional theory and implemented in powerful software packages, these methods permit efficient solutions of the electronic Schrödinger equation in the Born-Oppenheimer approximation and the computation of forces and energies for hundreds of atoms with thousands of electrons, which can then be used in molecular dynamics simulations [7], [8]. Currently, significant efforts are directed towards including excited electronic states and a consistent quantum mechanical description of the nuclear degrees of freedom into the simulations. Although far from complete (one cannot throw a few electrons and nuclei into a box yet and see what happens), these developments, initiated by Boltzmann and his contemporaries, are an important step towards the ultimate goal of deducing structural and dynamical properties of complex (and even living!) condensed matter from a mere knowledge of the chemical composition.

Beside molecular dynamics, the other computational pillar in condensed matter theory is Monte Carlo simulation [1], which has its roots in the ideas of Boltzmann and, particularly, Gibbs. In a Monte Carlo simulation one does not follow the real dynamics of the system in time, but rather samples random configurations according to the underlying phase space distribution. As alluded to by the name coined in the early 1950s by Metropolis and Ulam [9], [10], random numbers play a crucial role in the method and are used to carry out a biased random walk through phase space. As the Monte Carlo method is not limited by the natural dynamics of the system, one can dream up completely unphysical moves that dramatically increase the rate at which the configuration space is sampled as long as one makes sure that the target ensemble is

reproduced. This can be achieved by enforcing detailed balance, but of course comes at the cost that a dynamical interpretation of the simulation is no longer meaningful. Examples for such efficient algorithms include cluster moves designed to prevent the sampling from slowing down near criticality, and configurational bias Monte Carlo schemes [11]. The Monte Carlo method is, in principle, exact in the sense that for a given model no approximations are involved. Provided one runs the Monte Carlo simulation for a sufficiently long time, the correct phase space distribution is sampled and the calculated ensemble averages converge towards the true values. In general, the Monte Carlo method is limited to equilibrium states with known phase space density. In contrast, molecular dynamics simulations can be easily carried out in non-equilibrium situations for which the phase space distribution is usually unknown.

While molecular dynamics simulation is used today to carry on Boltzmann's program, it does not directly depend or build on any of his results. In contrast, the Monte Carlo method is based on the realization that time averages can be replaced by ensemble averages and on the ensemble theory that grew out of this insight. From a practical point of view, this represents a tremendous simplification since the complicated dynamics of many-particle systems can be completely ignored and the calculation of macroscopic properties be reduced to integrals over rather simple distribution functions. It is exactly this simplification of equilibrium statistical mechanics, which makes the Monte Carlo method one of the most powerful tools in condensed matter theory. It is often stated that the idea of ensembles in statistical mechanics goes back to Gibbs, but the basic concept of considering a large number of independent system copies and their distribution in phase space can be traced back to Boltzmann, as mentioned by Gibbs himself in the preface to his celebrated book on the "Elementary Principles in Statistical Mechanics" [12]. As pointed out by Cercignani<sup>1</sup> [15], in a paper from 1884 Boltzmann considers stationary statistical ensembles of many systems and calls them "Monode" [13]. Ensembles consistent with macroscopic equilibrium thermodynamics, i.e., ensembles for which  $\delta Q/T$  is an exact differential, he then calls "Orthode". Boltzmann carries on by showing that both what he calls a "Holode" (the *canonical ensemble* in Gibbs' terminology) and an "Ergode" (the *microcanonical ensemble* in Gibbs' terminology) belong to this class of "Monodes" (i.e., ensembles). But while the idea of statistical ensembles originated from Boltzmann (it is, however, quite possible that both Boltzmann and Gibbs came up with the idea independently, but the respective evidence is sketchy), it was Gibbs who formulated equilibrium statistical mechanics in a clear, systematic and eminently practical way making its application easy for later generations of researchers. (Incidentally, Gibbs also invented the name "Statistical Mechanics".) For a detailed and insightful account on the reception of the work of Boltzmann and Gibbs we refer the reader to the Boltzmann biography of Cercignani [15] and the book of Hoover [16].

Early Monte Carlo simulations were carried out in the canonical ensemble, or  $NVT$ -ensemble, which corresponds to a system with fixed particle number  $N$ , volume  $V$  and temperature  $T$ . Later, Monte Carlo simulations utilizing ensembles more appropri-

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<sup>1</sup>Note that, here, Cercignani cites the wrong article. Boltzmann considers ensembles (and, in particular, the microcanonical and canonical ensembles) in [13] and not in [14] as asserted by Cercignani.

ate for particular experiments were developed and applied to a wide variety of situations. Examples include simulation algorithms for the grand-canonical ensemble ( $\mu VT$ -ensemble), which describes systems with fixed volume  $V$  at temperature  $T$  in contact with a particle reservoir with chemical potential  $\mu$ , or the isobaric-isothermal ensemble ( $NpT$ -ensemble), which is appropriate for systems with fixed particle number  $N$  at pressure  $p$  and temperature  $T$ . In some cases, particularly for the calculation of free energies, it is even advantageous to sample generalized ensembles that do not correspond to a particular physical situation. Such sampling techniques, which include umbrella sampling [17] and Wang–Landau sampling [18], are collectively referred to as non-Boltzmann sampling as opposed to the Boltzmann sampling of physical ensembles. Monte Carlo methods are not limited, however, to ensembles in configuration or phase space. Recently, Monte Carlo techniques have been developed to sample ensembles of rare dynamical trajectories, which occur, for example, during the nucleation stage of a first-order phase transition, of conformational changes of biomolecules, or of chemical reactions between different species [19], [20], [21]. The success of Monte Carlo simulations in different ensembles has also provided the motivation to develop molecular dynamics methods capable of sampling other ensembles than the microcanonical, in which particle number  $N$ , volume  $V$ , and total energy  $E$  are conserved. Stochastic and deterministic “computer thermostats”, artificial modifications of the equations of motion designed to reproduce a particular ensemble [22], [23], [24], are now standard tools of the computer simulator. Such thermostats also play a particularly important role in the molecular dynamics simulation of non-equilibrium steady states, which are discussed in more detail in Section 7.

The field of molecular dynamics and Monte Carlo simulation, which by now are universal techniques to tackle a great variety of problems, is still growing at a fast pace. For an overview of current methodologies and applications we refer to the proceedings of a recent summer school [25]. The introduction to this collection of articles includes a very enlightening discussion of the significance of computer simulations for the statistical mechanics of condensed matter.

### 3 Chaotic motion and mixing in phase space

The relaxation of non-equilibrium states towards equilibrium as described by the Boltzmann equation requires mixing in phase space. For a classical Hamiltonian system evolving at constant energy, say a system of purely repulsive spheres undergoing elastic collisions, this implies that a set of initial conditions concentrated in a small fraction of phase space will eventually spread evenly over the whole energy shell. At first sight this requirement seems to be in contradiction with Liouville’s theorem according to which phase space volume is conserved under the action of the phase flow. However, as depicted schematically in the left panel of Figure 2, a small compact volume of initial conditions deforms into a complicated shape as time evolves while keeping its volume constant. Let us follow Boltzmann and imagine that the phase space is partitioned into little boxes. The evolving filaments grow into more and more boxes and, eventually,

spread all over the available phase space in such a way that the fraction of the original points located in an arbitrary box is proportional to the size of that box. If this happens, the system is said to be mixing.

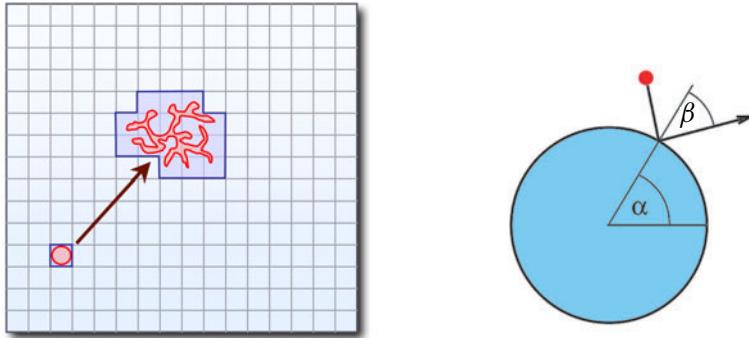


Figure 2. *Left panel:* Dispersion of a volume of initial conditions in phase space. *Right panel:* The Lorentz gas consists of a point particle moving at constant speed in an array of circular scatterers (see Figure 2, right panel) [26]. The motion of the particle consists of free flight segments on straight lines, interrupted by instantaneous collisions with the scatterers, when the particle is elastically reflected. At the collision the velocity component orthogonal to the surface at the collision point changes sign, the tangential component remains unchanged. Due to the convex shape of the scatterers, trajectories starting from neighboring points separated by  $\delta_0$  in phase space diverge exponentially in time.

For low dimensional systems this spreading in phase space can be easily visualized with a computer. Consider, for instance, the so-called Lorentz gas in two dimensions, which consists of a point particle moving at constant speed in an array of circular scatterers (see Figure 2, right panel) [26]. The motion of the particle consists of free flight segments on straight lines, interrupted by instantaneous collisions with the scatterers, when the particle is elastically reflected. At the collision the velocity component orthogonal to the surface at the collision point changes sign, the tangential component remains unchanged. Due to the convex shape of the scatterers, trajectories starting from neighboring points separated by  $\delta_0$  in phase space diverge exponentially in time:

$$\delta_t \approx \delta_0 \exp(\lambda t). \quad (1)$$

Here,  $\delta_t$  is the separation in phase space at time  $t$  and  $\lambda$  is called a Lyapunov exponent. This sensitivity to small perturbations of the initial conditions, which corresponds to a positive  $\lambda$ , is the defining feature of deterministic chaotic motion that is commonly observed in classical many-particle systems at sufficiently high temperature.

We can now observe how the exponential growth of small perturbations in phase space, also referred to as Lyapunov instability, causes spreading in phase space and mixing. To do this for the Lorentz gas, we consider a lower dimensional section of phase space which consists of the angles  $\alpha$  and  $\beta$ . They completely describe the state of the moving particle at the collisions with the periodically replicated scatterer. Each point in the two-dimensional phase space section spanned by these variables corresponds to a collision occurring at a particular point and with a particular velocity direction. The time evolution maps each collision point into the next one. We now apply the map defined in this way to a set of many initial conditions all located in a small region of

phase space, the black square in the top left panel of Figure 3. The map distorts the original set, contracting it in some directions but expanding it in others (center top panel). The area of this set, however, is unchanged. The sets resulting after 2, 4, 6, and 10 collisions are shown in subsequent panels of Figure 3 and clearly demonstrate the spreading. Eventually, it leads to a uniform distribution over all of the available phase space.

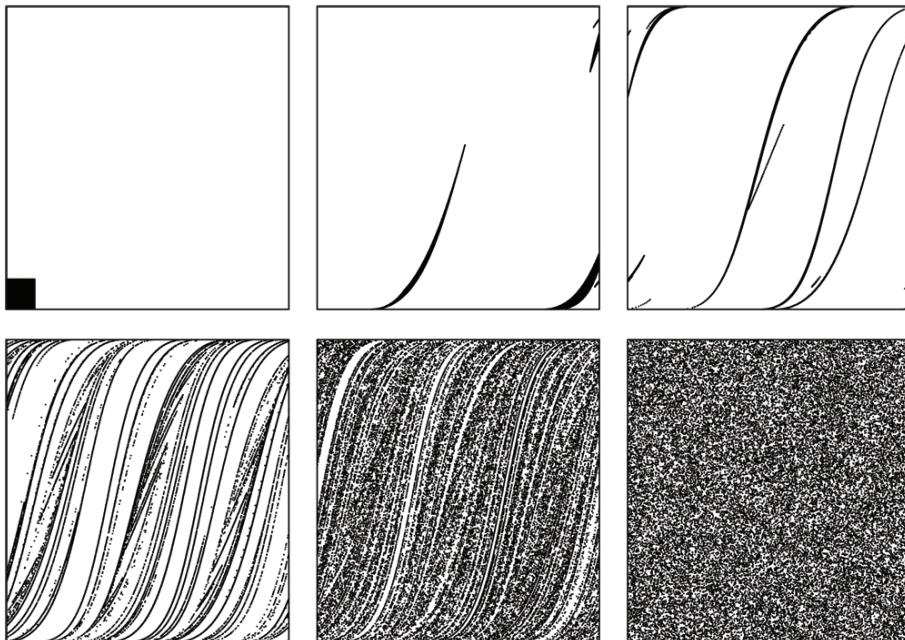


Figure 3. Spreading of initial conditions initially concentrated in a small part of the phase space of the Lorentz gas on a triangular lattice. Shown are sections of the phase space at the collisions of the moving particle with the replicated scatterer, where the angle  $\alpha$  is used on the  $x$ -axis and  $\sin \beta$  on the  $y$ -axis. The first plot in the upper left corner contains 100,000 points representing as many initial conditions. Subsequent plots correspond to phase space sections after 1, 2, 4, 6, and 10 collisions. The density of the scatterers is 4/5 of the close-packed density.

Since the phase space volume of the evolving set is conserved according to Liouville's theorem, it cannot be used to quantify the mixing process. Instead, one has to introduce some kind of coarse graining, for instance by partitioning the phase space into small boxes as depicted in the left panel of Figure 2. Initial points positioned in a single box will evolve and spread to more and more boxes, since the phase flow expands in some directions. From the coarse grained point of view the contraction simultaneously occurring in other directions is irrelevant. Eventually, all boxes are uniformly filled.

The spreading can be monitored with Boltzmann's  $H$ -function<sup>2</sup>.

$$H(t) = \sum_i f_i(t) \ln f_i(t) \quad (2)$$

where  $f_i(t)$  is the fraction of phase space points present at time  $t$  in box  $i$ . More than 60 years ago, Krylov predicted that the number of boxes  $N_t$  visited at  $t$  grows exponentially with a rate determined by the Kolmogorov–Sinai entropy  $h_{\text{KS}}$  (which turns out to be the sum of all positive Lyapunov exponents):

$$N_t \sim \exp(h_{\text{KS}}t). \quad (3)$$

This leads to an  $H$ -function which decays linearly with time [29], starting from its initial value zero. The slope is given by  $h_{\text{KS}}$ . Obviously, the linear decay comes to an end when all available boxes are filled, and  $H(t)$  becomes constant. It is worth pointing out that the function  $H(t)$  decreases only due to the coarse graining introduced by the partitioning of the phase space into finite-sized boxes. If the sum in equation (2) is replaced by a phase space integral,  $H(t)$  is constant in time for any arbitrary initial distribution  $f$ , as can be easily proved using Liouville's theorem. Krylov's hypothesis on the time behavior of the coarse grained  $H(t)$  was confirmed by computer simulations of the two-dimensional periodic Lorentz gas [30], in which case, due to the low dimension, the Kolmogorov–Sinai entropy is equal to the single positive Lyapunov exponent for this model. It is the Kolmogorov–Sinai entropy that really determines the rate of mixing in phase space and, hence, the approach to equilibrium. Such a behaviour is expected to hold also for high-dimensional systems. However, it is crucial in this case to consider the full many-particle distribution function and not projections to lower dimensions such as the single-particle distribution function in  $\mu$ -space considered by Boltzmann. In contrast to the case of the full phase space distribution, the characteristic time for the relaxation of single particle distribution functions is the collision time, the average time between successive collisions of a particle.

## 4 Ergodicity

Mixing in phase space is intimately related to the notion of ergodicity, another idea central to Boltzmann's work and to modern computer simulation. In an ergodic system, every point in phase space consistent with the thermodynamic variables describing the macroscopic state of the system is eventually visited. As a consequence, time averages can be replaced with appropriate ensemble averages, which often leads to great simplifications in analytical and numerical calculations. It was soon realized that for the equality of time and ensemble average the quasi-ergodic property is sufficient, which states that the system will come arbitrarily close to any point in phase space rather than visiting every point exactly. (As noted by Stephen G. Brush in his introduction

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<sup>2</sup>Although there is some indirect evidence that the capital letter “ $H$ ” in Boltzmann's “ $H$ -theorem” might have been intended to be a capital Greek Eta, there is no definite proof for this assertion [27], [28].

to Boltzmann's *Lectures on Gas Theory* [31], however, Boltzmann did not clearly distinguish between ergodicity and quasi-ergodicity.) It is quasi-ergodicity that permits us to calculate the properties of many-body systems via Monte Carlo simulation without the need to follow the detailed dynamics. Some of the earliest simulations carried out on the electronic computing machines available after World War II were devoted to test this hypothesis.

In 1953 Enrico Fermi, John R. Pasta und Stanislaw Ulam used MANIAC, von Neumann's computing machine installed in Los Alamos, to perform a numerical integration of the equations of motion (a molecular dynamics simulation) of a one-dimensional chain of particles with nearest neighbor interactions that were weakly non-linear [32]. (An account of the history of the Fermi–Pasta–Ulam simulation is given in Refs. [33] and [34].) The purpose of this calculation was to examine how the system evolves towards equilibrium starting from an initial state in which only one mode of the chain is excited, for instance a single sound mode. Fermi, Pasta and Ulam expected that due to the weak non-linear coupling between the particles the energy initially concentrated in one single mode would gradually spread to all other modes eventually leading to a fully equilibrated state. Contrary to this expectation, the scenario that Fermi, Pasta and Ulam observed to their great surprise was very different: instead of continuously thermalizing towards equilibrium, the system almost perfectly returned to its initial state after an initial spreading of the energy to other modes. Later simulations showed that such recurrences occur with even higher accuracy on longer time scales, and equilibrium is not achieved. This astonishing finding, motivated also by Boltzmann's ideas, led to many subsequent studies of non-linear dynamical systems, both theoretical and experimental, and spawned soliton theory [35]. Fermi himself was modestly proud of this work calling it a “minor discovery” [9].

From a computational point of view the pioneering work of Fermi, Pasta, and Ulam was important in various ways. Their work constituted the first “computer experiment” in which the role of the computer went beyond the mere calculation of mathematical expressions unpractical for evaluation with pencil and paper. Instead, their studies established computer simulation as a powerful instrument to explore new ideas and to obtain truly new physical insight. Also remarkable is the fruitful interaction of simulation and theory that arose from these early simulations and the impetus they gave to the development of the theory of non-linear dynamics.

Ergodicity (or quasi-ergodicity) is also a recurrent issue in the application of computer simulation to complex atomistic and molecular systems. For instance, deterministic computer thermostats are often used to control temperature in molecular dynamics simulations of equilibrium and non-equilibrium states. These thermostats replace large heat baths by one or a few degrees of freedom that are appropriately coupled to the equations of motion of the system. This will be discussed further in Section 7. However, deterministic thermostats are often unable to equilibrate the dynamics of strong harmonic degrees of freedom [36], [37]. Particular techniques using higher momentum moments [37] or chains of coupled thermostats [38] have been developed to overcome this problem. Insufficient sampling, i.e. lack of ergodicity, can also occur in Monte Carlo and molecular dynamics simulations, if high energy barriers separate important

regions of configuration space. Enhanced sampling techniques such as multicanonical sampling [39] and parallel tempering [40] may be used to overcome this limitation.

## 5 Hard spheres: entropy, freezing and long time tails

One of the fundamental tasks of equilibrium statistical mechanics is to determine the equation of state and the phase diagram of a given substance from a knowledge of its microscopic constituents. The Second Law of Thermodynamics, together with Boltzmann's statistical interpretation, provides us with the tools to do that either analytically or numerically. The first statistical mechanical theory that successfully mapped out a non-trivial phase diagram was the theory of van der Waals, which correctly predicts the condensation of vapor into a liquid and even yields a qualitative description of critical phenomena. In his *Lectures on Gas Theory* [31], Boltzmann devotes several chapters to this topic and derives the van der Waals equation using Clausius' virial concept. Anticipating later statistical mechanical theories of the liquid state [41], [42], Boltzmann separates short range hard-sphere repulsion from long range attractive interaction. For the hard sphere contribution, he then proceeds by considering the “available space”, i.e. the volume from which a specific particle is not excluded due to the presence of all other remaining particles. In a very elegant way, Boltzmann writes a first order approximation for this quantity that he then further refines by estimating the overlap of the exclusion volume of different spheres. The resulting expression is a virial expansion involving what we now call the third virial coefficient. Combining this result with the virial calculated for the van der Waals cohesive interaction, Boltzmann finally obtains the van der Waals equation. The next-order correction, i.e. the fourth virial coefficient was calculated analytically by Boltzmann with remarkable physical insight (see [43] for an interesting account of the history of the fourth virial coefficient, and [44] for a history of the development of equations of state from kinetic theory). After Boltzmann, progress in the virial expansion of the equation of state for hard sphere systems has been made only numerically. Although systematic procedures such as the Mayer cluster expansion for obtaining higher order virial coefficients are available, the expressions quickly become so complicated that to date all virial coefficients beyond the fourth (and at least up to the tenth) are known only from Monte Carlo integration [45]. Since the hard sphere equation of state is known with high accuracy from the dilute gas regime to close packing, the motivation to be further concerned with the series expansion (and, in particular, with the analytical derivation of virial coefficients) is rather limited.

The van der Waals equation of state and its refinements derived by Boltzmann predict, when augmented with a Maxwell construction, a first order phase transition between a low density gas and a high density liquid. This transition does not occur in the absence of the long range attractive forces postulated by van der Waals. For purely repulsive hard sphere systems, however, a different question arises. It is clear that at low densities hard spheres exist as a disordered gas. At high densities near close packing, on the other hand, hard spheres must be arranged on a regular lattice such as the face-centered-cubic or the hexagonal-close-packed lattices. Does this

transition from a low density gas to a high density solid occur continuously or discontinuously? In other words, is there a hard sphere freezing transition to a crystalline solid with long range order as first predicted by Kirkwood in 1951 [46]? In the mid-1950s this was an important open question, but no theoretical tools were available to derive the properties of phase transitions from the first principles of statistical mechanics [47]. The virial expansion pioneered by Boltzmann does not give any indication about the existence of such a transition. So it was no surprise that at a symposium on “The many-Body Problem” held 1957 at the Stevens Institute of Technology in Hoboken, New Jersey, during a round table discussion lead by G. E. Uhlenbeck on general topics of statistical mechanics, a vote taken among prominent scientists (including several Nobel laureates) about this question ended evenly [48]. The hesitation of half of the audience is understandable, because it is indeed surprising that purely repulsive particles can form a stable crystal. The question was finally settled in favor of the existence of the fluid-solid transition on the basis of now famous molecular dynamics simulations by Alder and Wainwright [49] and Monte Carlo simulations by Wood and Jacobson [50].

These simulations, and later ones by Hoover and Ree [51], in which the entropy of both phases was computed, showed that for packing fractions in the range  $\phi = 0.49\text{--}0.55$  (the packing fraction  $\phi$  is the fraction of volume filled by the hard spheres) a disordered fluid phase with packing fraction  $\phi = 0.49$  coexists with an ordered solid phase with  $\phi = 0.55$ . While for packing fractions below  $\phi = 0.49$  the fluid is the more stable form, at densities between  $\phi = 0.55$  and close packing occurring at  $\phi = \pi/\sqrt{18} \approx 0.74$  the hard sphere system exists as a solid. Both the solid and the fluid branch of the equation of state can be extended into the respective metastable region (see Figure 4), which indicates that the hard sphere freezing transition is indeed first order. Recent ex-

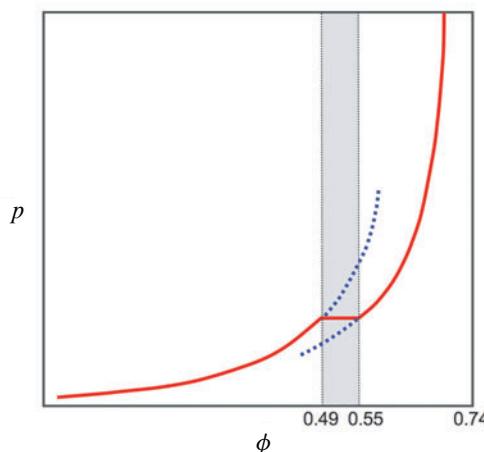


Figure 4. Pressure  $p$  as a function of the packing fraction  $\phi$  for a system of hard spheres. The gray area indicates the coexistence region and the dotted lines are the metastable branches of the equations of state for the fluid and the solid phases.

perimental and computational studies have focused on the related intriguing question, whether identical objects of a given geometry may be packed more densely when they are arranged in a random rather than a crystalline fashion [52]. In three dimensions, the highest possible random packing fraction for spheres is  $\phi = 0.64$ , considerably smaller than  $\phi = 0.74$  for the crystalline closed packed structure. Interestingly, there are indications that in dimensions higher than 57 (!) the situation reverses and random packing yields a higher density than crystalline packing [53].

An interesting aspect of the hard sphere freezing transition is that it is purely entropic. To see what that means we need to consider the thermodynamics of the liquid-solid transition. We know that according to the Second Law of Thermodynamics a system with given volume  $V$  and temperature  $T$  exists in a state for which the Helmholtz free energy

$$F = U - TS \quad (4)$$

is a minimum. In other words, the thermodynamically stable phase is that one with the lower Helmholtz free energy. Other phases with higher free energy may be metastable but they tend to transform into the more stable phase provided this is kinetically possible. As stated in the famous inscription engraved on Boltzmann's tombstone in Vienna's central cemetery,

$$S = k \log W, \quad (5)$$

the entropy  $S$  is proportional to the logarithm of the number of states  $W$  accessible to the system. (Incidentally, this equation, expressed by Boltzmann only in words, was explicitly written down later by Planck.) Boltzmann's expression for the entropy is the link between statistical mechanics and thermodynamics and it provides a precise prescription on how to calculate the entropy for a given microscopic model. The general intuition now is that for an ordered system a smaller number of states is accessible than for a disordered system and, hence, the entropy of the ordered system should be lower than that of the disordered one. Together with the expression of the Helmholtz free energy (see equation (4)), this suggests that for any particular substance the transition from the disordered liquid to the ordered solid can only occur if the lower entropy of the ordered crystal is compensated by a sufficiently large loss in energy.

This scenario indeed describes some transitions, but in many cases this rather naive reasoning based on associating low/high entropy with apparent order/disorder is inaccurate, and it is entropy that drives the transition rather than energy. This is particularly evident for the hard sphere freezing transition. Since in the hard sphere system particles do not overlap due to the infinitely high interaction energy at contact, the total potential energy of the system vanishes for all possible configurations. Hence, the internal energy  $U$  is just the kinetic energy and, as in the ideal gas, is a function of temperature only. Thus, along an isotherm, the only change in free energy is due to the changing entropy which can be determined with high accuracy from computer simulations (since the entropy is a measure for the available phase space volume and cannot be written as an ensemble average of a dynamical variable, advanced simulation techniques such as thermodynamic integration have to be used). While for packing fractions below  $\phi = 0.49$  the fluid has the higher entropy, for packing fractions above  $\phi = 0.55$  the

solid is entropically favored and, hence, the thermodynamically stable phase. For intermediate packing fractions, the lower density fluid coexists with the higher density solid. The result that the solid, which we usually perceive as “ordered”, has a higher entropy than the disordered liquid is slightly counterintuitive and demonstrates that one should be careful in relating high entropy with disorder (of course, if one *defines* disorder via the number of accessible states, no inconsistencies arise). In the case of the hard sphere system at high densities, the solid is the thermodynamically stable phase, because in the regular crystalline structure more configuration space is available. Other transitions also have very important entropic components including the isotropic-nematic transition of liquid crystals, the phase separation of binary mixtures, protein crystallization and entropic forces in general [54]. In all these cases, computer simulations have played a decisive role in elucidating the complex physics underlying these processes.

Recently, non-Boltzmann Monte Carlo simulation algorithms have been developed [18], [55], which permit a rather direct calculation of the entropy  $S(E)$  as a function of the energy  $E$  from the density of states  $g(E)$ . The basic idea of these so-called flat-histogram methods is to sample a phase space density  $\rho(H(x))$ , which depends only on the system energy  $H(x)$ . This phase space density  $\rho(H(x))$  is not constant but evolves in time in a particular way. Initially, one starts with a guess for the dependence of  $\rho$  on  $H$ , using, for instance, a constant. As the simulation proceeds,  $\rho(H)$  is adapted iteratively in a way such that all system energies in a certain range occur with equal likelihood, i.e., the energy histogram is flat. When flatness is achieved, the phase space density is inversely proportional to the density of states,  $\rho(H(x)) \propto 1/g(H(x))$ , and the entropy is given, except for a constant, by  $S(E) = -k_B \ln \rho(E)$ . Flat-histogram methods are of very general applicability. Recently, this idea has been used for the calculation of coarse grained Landau–Ginzburg free energies via Monte Carlo simulations in Fourier space [56]. Dynamical versions of flat-histogram sampling, such as the metadynamics method [57], have been proven very useful for the exploration of the configuration space of complex systems.

While the early work of Alder and Wainwright and of Wood and Jacobsen, as well as other computer simulations performed later, unequivocally confirmed the existence of the hard sphere freezing transition, another related and seemingly simpler question proved much more persistent, namely that about the structure of the hard sphere solid. It took about forty more years to figure this out on the basis of computer simulations. At high densities, the hard sphere solid is expected to exist in a structure that supports close packing such as the face-centered-cubic (fcc) structure or the hexagonal-close-packed (hcp) structure, which differ in the particular way hexagonal close-packed layers of spheres are stacked on top of each other. The question now is: is the fcc or the hcp structure the more stable phase? Or, in other words, which one of the phases has the higher entropy? While in both phases the first neighbor shell of each particle is identical, the fcc and hcp structures differ in their second neighbor shell and beyond. It is this difference that causes the entropy of the two phases to be different. Early analytical calculations based on a series expansion indicated that the hcp structure has a higher entropy than the fcc structure [58]. Computer simulations carried out between 1960 and 1990 gave inconclusive results which only demonstrated that the entropy

difference per particle, if any, is very small compared to  $k_B$ . Using the so-called Einstein crystal technique, a thermodynamic integration method based on a reference system with particles attached to lattice sites with harmonic springs, and sophisticated multicanonical sampling techniques, it was finally shown in the late 1990s that the fcc structure has the highest entropy [59], [60]. The entropy difference between fcc and hcp, which slightly increases as the density is raised from melting to close packing, has a value of about  $10^{-3} k_B$  with error bars of the order of 10%. The fcc-structure has also a higher entropy than all other random and periodic stacking sequences [61].

Computer simulations have not only helped to understand the structure of systems with hard interaction, but also their dynamics. One early discovery concerns the appearance of vortex-like flow patterns around moving particles in the hard sphere fluid [62]. Such collective vortices effectively store the momentum of a thermal particle and return it to the same particle at a later time, thus causing autocorrelation functions to decay algebraically for long times rather than exponentially as was originally expected from kinetic theory under the assumption of uncorrelated binary collisions. Motivated by these computational results of Alder and Wainwright, Cohen and Dorfman later reproduced the algebraic long-time behavior of correlation functions with kinetic theory and traced it back to the importance of ring collisions involving the correlated motion of many particles [63]. The vortices observed by Alder and Wainwright are consistent with predictions of continuum hydrodynamics indicating that, in an averaged sense, hydrodynamics remains valid all the way down to the atomic length scale.<sup>3</sup> This conclusion was also supported by later simulations [64]. More recently, computer simulations of the dynamics of hard sphere systems have concentrated on the nucleation of the stable solid phase from the metastable fluid generated by sudden compressions. As already discussed by Boltzmann in the context of the van der Waals theory [31], metastable phases may have macroscopic lifetimes before the phase transition occurs and the thermodynamically stable phase forms. Qualitatively, this phenomenon can be understood by classical nucleation theory, which asserts that the phase transformation occurs via the formation of a critical nucleus [65]. Creation of the interface between the nucleus of the stable phase surrounded by the metastable phase carries a cost of free energy, such that this process initially raises the free energy. Thus, most small crystalline clusters formed by random fluctuations decay. Only when a rare fluctuation produces a cluster sufficiently large for the volume term, related to the lower chemical potential of the stable phase, to take over, can the nucleus spontaneously grow and initiate the phase transition. Recent computer simulations also showed that already for packing fractions  $0.42 < \phi < 0.49$ , well below the freezing transition of the hard sphere fluid, a structural precursor to the development of long-range order exists [66]. It manifests itself as a shoulder in the second peak of the radial distribution function and is a consequence of crystalline domains commensurate with those in the crystal at the melting point ( $\phi = 0.55$ ). Similar features have been experimentally observed for several simple liquids.

A quantitative understanding of nucleation and growth from first principles is cur-

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<sup>3</sup>However, the transport coefficients depend on the wave vector in this case.

rently attainable only with computer simulations. Frenkel and collaborators recently developed new and efficient computational methods employing advanced sampling techniques such as parallel tempering [40] to study the thermodynamics and kinetics of the nucleation process, and applied them to the nucleation of the hard sphere solid [67]. These and other new computational studies of the structure and dynamics of hard sphere systems are far from being of only academic interest. Rather, hard spheres are excellent models for colloidal systems that are currently studied experimentally in various settings. Using advanced experimental techniques such as confocal microscopy [68], it is now possible to study these systems particle by particle. Therefore, colloidal systems are a fascinating new test bed for statistical mechanical theories.

## 6 Fluctuation theorems and the Second Law

“The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability”. With this quote of Gibbs [69], Boltzmann opens the Foreword to Part II of his *Lectures on Gas Theory* [31]. Gibbs’ quote is from his memoir “On the Equilibrium of Heterogeneous Substances” in which, among other things, he discusses the entropy increase which occurs when two distinguishable gases mix. Clearly, both Gibbs and Boltzmann, as they repeatedly expressed, were fully aware of the fact that the tendency of the entropy to increase as the system relaxes towards equilibrium is an average property and that, particularly at small time and lengths scales, fluctuations contrary to this macroscopic law are possible. As new experimental tools become available to probe and manipulate small systems ranging from biomolecules and molecular motors to carbon nanotubes and nanocrystals, a quantitative understanding of these fluctuations already envisioned by Boltzmann and Gibbs is crucial for further progress.

We had to wait for over 100 years, however, for quantitative relations to emerge which describe such fluctuations in various non-equilibrium situations. These relations, now known as fluctuation theorems [70], [71], [72], essentially quantify the probability of trajectories with negative entropy production relative to that of trajectories with positive entropy production. The entropy production is related to the heat released to or absorbed from the environment. As the heat transfer is an extensive property, for macroscopic systems this relative likelihood is overwhelmingly tilted towards entropy production in agreement with the Second Law. This result also bears significance for the resolution of the so-called “reversibility paradox” raised by Joseph Loschmidt in 1876 as a reaction to Boltzmann’s monumental 1872 paper. Loschmidt’s objection was based on the observation that for a dynamics that is time-reversal invariant, trajectories must also exist along which the entropy decreases. According to the fluctuation theorems, such entropy reduction episodes do indeed occur, but with a probability that practically vanishes for macroscopic systems.

For the development of the fluctuation theorems, which can be viewed as an extension of Boltzmann’s statistical interpretation of the Second Law of Thermodynamics, computer simulations were extremely important. The first quantitative study of entropy-reducing fluctuations was performed using molecular dynamics simulations of

a sheared fluid in a non-equilibrium steady state [73]. Closely related to the fluctuation theorems is the Jarzynski equality [74], which relates equilibrium free energies to the statistics of work carried out on a system during non-equilibrium transformations. In the development of this exact result, computation played a slightly different role than for the fluctuations theorems, for which the results of computer simulations provided the motivation. In contrast, Jarzynski's incentive to derive his equality originated in the desire to develop an efficient computational algorithm for the calculation of free energies. An approximate precursor of Jarzynski's method were finite-time switching approaches [75], [76], in which upper and lower bounds to the free energy difference are obtained from the work carried out, while a system is switched irreversibly between the two states of interest. Jarzynski then realized that it is possible to determine exact free energy differences from such non-equilibrium trajectories along which the system departs strongly from equilibrium. To be more specific, imagine a system with a Hamiltonian  $H(x, \lambda)$  depending on an external parameter  $\lambda$  that can be controlled, for instance the position of a piston sealing a gas filled cylinder. Here,  $x$  denotes all microscopic degrees of freedom of the system. The controlled evolution of  $\lambda(t)$  is called a protocol. Different values of  $\lambda$  correspond to different macroscopic states which may differ in free energy:

$$\Delta F = F_B - F_A = -k_B T \ln \frac{\int dx e^{-\beta H(x, \lambda_B)}}{\int dx e^{-\beta H(x, \lambda_A)}}. \quad (6)$$

Now, if one switches the external parameter from an initial value  $\lambda_A$  to a final value  $\lambda_B$  in a finite time  $\tau$  and the system evolves according to the rules of the underlying dynamics, the work  $W = \int_0^\tau (\partial H / \partial \lambda) \dot{\lambda} dt$  is carried out on the system. According to Clausius' maximum work theorem, which is a consequence of the Second Law of Thermodynamics, the average work  $\langle W \rangle$  carried out by changing an external parameter is larger than the difference of the Helmholtz free energy of the two equilibrium states corresponding to the initial and final value of  $\lambda$ ,

$$\langle W \rangle \geq \Delta F. \quad (7)$$

The angular brackets denote an average over many realizations of the switching process starting from canonically distributed initial conditions. The equality holds only if the transformation is carried out reversibly, i.e., if the system is in equilibrium at all times during the transformation. In 1997 Jarzynski proved under quite general conditions that, if the average is taken for the exponential of the work rather than the work itself, the Clausius inequality is transformed into an equality:

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F). \quad (8)$$

Today, several proofs of the Jarzynski identity exist [74], [77], [78], [79], [80], [81], [82]. Due to the convexity of the exponential function, the maximum work theorem follows as a corollary from this equality. Remarkably, the Jarzynski equality is exact even if the system is violently driven away from equilibrium. In this case, the average

work carried out during the non-equilibrium process may by far exceed the equilibrium free energy difference. Nevertheless, the equality (8) is saved by the occurrence of very rare work fluctuations that provide significant contributions to the exponential work average.

An important extension of Jarzynski's equality was provided by Crooks [78], who compared the probability distribution  $P_F(W)$  of the work  $W$ , carried out during the switching process from  $A$  to  $B$ , to the work distribution  $P_R(W)$  for the switching from  $B$  to  $A$  with the time reversed protocol. Crooks found that

$$\frac{P_R(-W)}{P_F(W)} = \exp[-\beta(W - \Delta F)]. \quad (9)$$

As the fluctuation theorems mentioned above, also this so-called Crooks fluctuation theorem provides a quantitative relation for the probability of fluctuations that seemingly violate the Second Law. The Jarzynski equation follows immediately from the Crooks fluctuation theorem. Both the Jarzynski equality and the Crooks fluctuation theorem can be easily translated into computer algorithms for the calculation of free energies. Whether such fast switching methods can be competitive compared to conventional approaches such as umbrella sampling or thermodynamic integration [11] is an open question, but there are indications that they might not [4], [5]. The true significance of these results, however, lies in the fact that they provide a rigorous way to analyze and interpret experiments carried out far away from equilibrium [83], [84]. As some of the few known exact relations for non-equilibrium systems, the fluctuation theorems briefly discussed in this section may prove crucial for the development of a unified theory of non-equilibrium processes at small length and time scales.

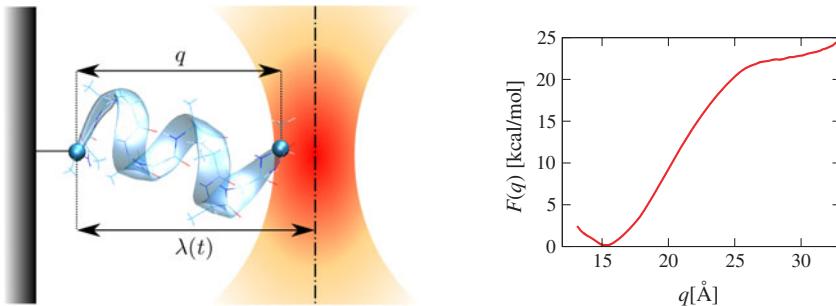


Figure 5. Modern micromanipulation equipment permits to exert well defined forces on single molecules and probe the free energetics of selected degrees of freedom. On the left-hand side a deca-alanine molecule is stretched by a laser trap translated at constant speed (graphics by Harald Oberhofer, University of Vienna). The free energy  $F(q)$  shown on the right-hand side as a function of the end-to-end distance  $q$  was obtained by analyzing the work performed on the system during the non-equilibrium stretching process [79], [85].

## 7 Fractal phase space distributions and irreversibility of nonequilibrium stationary states

Boltzmann's probabilistic explanation of the irreversibility of macroscopic processes applies to closed systems which do not interact with the outside world. He repeatedly pointed to the significance of the initial conditions, if the system is released from a non-equilibrium state to relax towards equilibrium. The question arises, what makes the equilibrium state so unique in view of the time-reversible nature of the (Newtonian) equations of motion for the particles? Pusz and Woronowicz proved that equilibrium states are "passive", which means that no mechanical work may be gained from an isolated system in such a state by applying an external adiabatic perturbation [86], [87]. The notion of passivity is a particular formulation of the Second Law and is equivalent to the statement that the system cannot be used as a perpetual motion machine of the second kind. But what are the "active" states which may give rise to fluctuations violating the Second Law, and how are they distributed in phase space? If the concept of passivity is applied to trajectories of pure states, i.e. points in phase space, it has been shown for an ensemble of non-interacting harmonic oscillators that the active states have measure zero and are distributed on a Cantor-like fractal set in phase space [88]. Most likely, a similar picture prevails also for more realistic systems, although we do not know of any proof. For the first time, we encounter fractal objects in phase space in connection with the Second Law.

Closer to laboratory experiments are systems in stationary nonequilibrium states. Computer simulations turn out to be essential for the study of transport properties in this case. Nonequilibrium states are generated by the application of an external perturbation, which may be either mechanical (external fields) or thermal (velocity or temperature gradients). Since the perturbation performs work on the system which is eventually dissipated into heat, a thermostating mechanism is required to achieve a stationary state. A prototypical example is a gas sandwiched between two huge blocks of copper at different temperatures acting as thermostats such that a stationary heat flow develops from the warm to the cold block. However, for computer modeling, the "huge blocks" pose a serious obstacle, since they add (too) many thermostated degrees of freedom to the problem. An ingenious dynamical scheme may be used to avoid the introduction of so many additional variables. It consists in replacing a "block" by a small number of thermostat particles and adding a constraint force  $-\zeta(t)p_i$  to their equations of motion, which follows from Gauss' principle of least constraint [89], [90]. Here,  $p_i$  is the momentum of the thermostat particle, and  $\zeta(t)$  is a time-dependent friction, one for each thermostat. In this way, the kinetic energy (or internal energy) may be controlled, either instantaneously (Gauss thermostat) or in a time-averaged sense (Nosé–Hoover thermostat) [91], [92].

The key observation is that Gauss and Nosé–Hoover thermostats leave the equations of motion invariant with respect to time reversal. This means that for any computer-generated trajectory obtained in the forward direction of time, the same sequence read backwards in time with the sign of the momenta and the friction variables reversed is also a solution of the original motion equations. Nevertheless, a computer simulation

of a thermostated nonequilibrium system always gives a positive time-averaged friction variable (or a positive sum of time-averaged friction variables, if more than one thermostat is involved), if the evolution is followed long enough either in the positive or negative direction of time. The system always behaves irreversibly on a macroscopic time scale in accordance with the Second Law although the microscopic dynamics is time reversible [93], [94], [95], [96].

To understand this behaviour, we consider as a simple example the Lorentz gas introduced in Section 3. But now the point particle moving in a periodic array of circular scatterers in two dimensions is also subjected to a constant force  $E$  acting in the positive  $x$  direction, and a Gauss thermostat is used to keep the kinetic energy exactly constant. Between collisions, the particle still moves with constant speed but not on straight lines anymore (left panel of Figure 6). On average, it experiences a

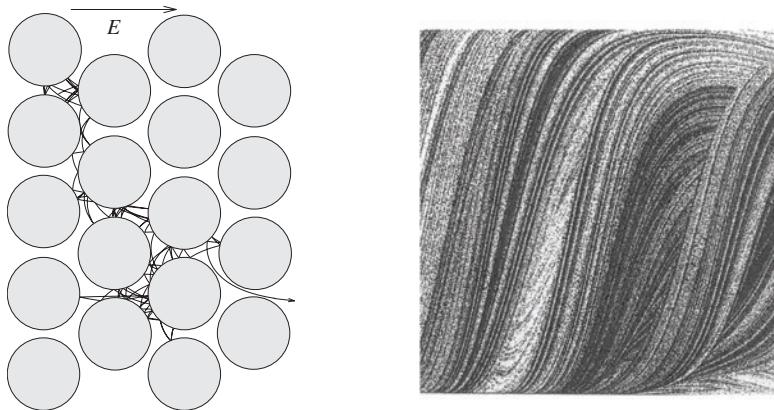


Figure 6. *Left panel:* Geometry and short trajectory of a periodic driven Lorentz gas. In addition to the elastic reflections, a constant force  $E$  and a Gauss thermostat acts on the wandering point particle. *Right panel:* Section of the phase-space probability in the stationary nonequilibrium state. The same coordinates as in Figure 3 are used.

constant drift velocity in the direction of the perturbing force. A section of the phase space density  $f$  is shown in the right panel of Figure 6 for this case. Whereas in the absence of the perturbation the points are uniformly distributed as in the bottom-right panel of Figure 3, the nonequilibrium stationary state of Figure 6 is characterized by a multifractal phase-space distribution  $f$ , which is singular in every point. The following important chain of relations holds [97]:

$$\left\langle \frac{d \ln \delta V}{dt} \right\rangle = - \left\langle \frac{d \ln f}{dt} \right\rangle = - \frac{\dot{S}_{\text{irr}}}{k_B} = \sum_{l=1}^D \lambda_l = -\langle \xi \rangle < 0. \quad (10)$$

The first two equalities state that any infinitesimally-small phase volume  $\delta V$ , co-moving with the phase flow, shrinks on average and leads to an attractor and a multifractal probability distribution  $f$  in phase space as shown in Figure 6. Furthermore, the

rate of irreversible entropy production,  $\dot{S}_{\text{irr}}$ , is constant and positive as expected for a stationary system, and is proportional to the time-averaged friction, which determines the rate with which heat is extracted by the thermostat. It is also proportional to the sum of all Lyapunov exponents,  $\sum_{l=1}^D \lambda_l$ , where  $D$  is the dimensionality of the phase space, which is four in this particular model (not taking the conservation of the energy into account which reduces the effective phase space dimension by one). Finally, the last inequality assures that the associated transport coefficient, a conductivity, is positive in accordance with the Second Law.

The fractal nature of the phase-space probability density  $f$  provides the key for understanding irreversibility in this case. Both forward and backward in time, a phase space trajectory converges to this attracting set characterized by a negative sum of Lyapunov exponents. A time reversal transformation maps this attracting set into a repellor which is also a fractal set, but with a positive Lyapunov exponent sum. Therefore, the repellor is much more unstable than the attractor, and the phase flow always leads from the repellor to the attractor regardless of the direction of time. This constitutes irreversibility on a macroscopic time scale.

Let us add a few comments concerning this remarkable result. The chain of relations in equation (10) and the conclusions drawn from them are not particular to this specific model, but – with very slight generalizations – apply to all stationary nonequilibrium systems with dynamical time-reversible thermostats. Through the appearance of the Lyapunov exponents, it establishes a link between transport theory and dynamical systems theory and opens a new way to understand irreversibility and the Second Law [98]. It should be noted that this insight was first obtained by computer simulations [93] with theoretical verification for simple cases following later [99]. We like to think that Boltzmann would have approved of these results which extend his way of thinking to a wide class of dynamical systems in nonequilibrium stationary states.

Although these results are appealing and robust with respect to the choice of the dynamical thermostats and details of the computation, they suffer from the fact that this kind of thermostats cannot be realized in a laboratory experiment. At present, there is great theoretical activity trying to extend these ideas and concepts to the general case of stochastic constraints and boundaries.

## 8 The Boltzmann equation

Boltzmann's landmark paper of 1872 [100] had an enormous influence on the development of statistical mechanics for multiple reasons. In that paper, Boltzmann derived an equation, now known as the Boltzmann equation, for the time evolution of the single particle distribution function  $f(\mathbf{x}, \mathbf{v}, t)$  in  $\mu$ -space. In the absence of external forces, the Boltzmann equation may be written in simplified form as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{x}} = \frac{\partial f}{\partial t} \Big|_{\text{coll}}. \quad (11)$$

While the left-hand side of this equation describes the free streaming of the particles, the right-hand side takes into account the effect of intermolecular collisions. Neglecting

correlations, Boltzmann's famous “Stoßzahlansatz”, or hypothesis of molecular chaos, permits to write an explicit integral for the collision term  $\partial f / \partial t|_{\text{coll}}$  that depends only on single particle distribution functions and not on higher ones. In this approximation, the collision integral consists of a loss and a gain term due to molecules removed from, or injected into, a given  $\mu$ -space element by the collisions. The Boltzmann equation is an approximate but nevertheless very complicated integro-differential equation. It can be solved analytically only by applying further approximations. Even then, its solution is not straightforward and it took over 40 years before Chapman and, independently, Enskog succeeded in deriving from it the viscosity of a dilute gas [44]. The macroscopic Navier–Stokes equations for fluid flow follow from the Boltzmann equation provided the deviations from local thermodynamic equilibrium are small.

Although the Boltzmann equation was developed to understand the properties of dilute gases in and away from equilibrium and, in this way, to support the atomic hypothesis so vigorously promoted by Boltzmann, its significance extends far beyond this particular application. Historically, one important point is that the Boltzmann equation was the first equation of motion for a probability distribution. The equations of Smoluchowski, Fokker and Planck, Kolmogorov, etc. grew out of this probabilistic approach and are currently used to describe a wide range of phenomena in physics, chemistry, biology, and even in the social sciences. The applications go far beyond those envisioned by Boltzmann when he wrote down his equation [101], [102]. Also, Boltzmann's  $H$ -theorem derived from the Boltzmann equation initiated the discussion on irreversible behavior arising from time-reversible equations of motion. This discussion still persists to the present day as was mentioned briefly in Section 6 in connection with recent fluctuation theorems, and in Section 7, where we sketched a scenario for nonequilibrium systems in stationary states. Finally, the Boltzmann equation provides an elegant way to derive equilibrium distribution functions such as the famous Maxwell–Boltzmann distribution in momentum space.

From a computational point of view, several modern simulation techniques, particularly in the field of fluid dynamics, are based on Boltzmann's stochastic stream-and-collide idea [103], [104], [105], [106], [107], [108], [109]. At first sight, however, it is not immediately clear what the advantages of such a perspective are. After all, the exact time evolution of an atomistic system can be followed in detail using molecular dynamics simulations, and all relevant microscopic and macroscopic information can be extracted from them. While this is true in principle, such simulations are limited by the available computing resources both in the accessible length and time scales. Running on modern computer equipment, molecular dynamics simulations can be used to follow dense atomistic systems with linear extensions of up to tens of nanometers for times up to tens of nanoseconds. Phenomena occurring on longer length and time scales are outside the reach of present-day molecular dynamics methods. Attempts to extend these limitations have led to new computational methods which are based on the Boltzmann equation and, thus, emphasize its significance even today. These methods use coarse graining of the system's dynamics in a way which is consistent with macroscopic hydrodynamics as embodied in the Navier–Stokes equations.

Whereas in macroscopic hydrodynamics the moving fluid is represented by con-

tinuous fields related to the conserved quantities, computational methods based on the Boltzmann equation retain some atomistic features, however far less so than detailed molecular dynamics simulations. The underlying assumption of all these methods is that for the large scale flow, which arises from the collective motion of many particles, the details of the microscopic collision dynamics are irrelevant. In the direct simulation Monte Carlo method (DSMC) of Bird [103], for instance, binary collisions between particles still occur, but the collisions are determined statistically rather than from the deterministic dynamics of the system. In this method, the main idea is to decouple the motion of the “particles”, each possibly representing many real atoms or molecules, from their collisions. To do this while maintaining some crude spacial relations, space is partitioned into cells. The dynamics of the particles then consists of two steps: a free flight part, during which the particles move deterministically in a force-free way, and a collision part that takes into account particle interactions. The collisions are carried out by selecting pairs of particles at random from the same cell with a probability depending on their relative velocity. The collision parameters are then selected from appropriate distributions, and the collision is completed according to the rules of Newtonian mechanics for the selected random parameters. Energy and momentum are conserved during these collisions, a necessary requirement for hydrodynamic behavior to arise in the long wavelength limit. The statistical treatment of the collisions is equivalent to Boltzmann’s assumption of molecular chaos and, hence, the same limitations apply. The direct simulation Monte Carlo method has been used to address problems ranging from the dynamics of rarefied gases, for instance around a spacecraft re-entering the atmosphere, to growth processes of thin films [104], [110].

Perhaps even closer to the Boltzmann equation is the lattice Boltzmann method where one considers mesoscopic particles (i.e., each particle is thought of consisting of many microscopic particles) evolving on a regular lattice [108], [109]. Historically, the lattice Boltzmann method emerged from lattice gas cellular automata, in which particles exist with discrete velocities on the sites of a lattice. In these models, multiple occupation of lattice sites is possible but is limited to a maximum number. The fictitious particle dynamics proceeds in discrete time steps, and during each step particles move from one lattice site to another depending on their current velocities (this is the streaming step of the dynamics). At the lattice sites, particles interact and change velocities according to collision rules that guarantee the conservation of total energy and momentum. Remarkably, one can show that despite of these drastic simplifications the macroscopic Navier–Stokes equation for fluid flow arises in the continuum limit, provided the underlying lattice has the proper symmetry [111]. Although lattice gas cellular automata can be used to simulate hydrodynamic flow, they have some shortcomings, chiefly among them the statistical noise stemming from the discrete nature of the occupation numbers. These limitations were overcome by introducing the lattice Boltzmann method which differs from lattice gas cellular automata mainly by the replacement of the discrete occupation numbers with continuous populations representing ensemble averages. This eliminates statistical noise to a high degree. Today, the lattice Boltzmann method is used widely to study phenomena ranging from turbulence, fluid flow in porous media, and aerodynamics, to nanoscale hydrodynamics and

hydrodynamic interactions in colloids. Complex boundary conditions can be easily implemented in lattice Boltzmann simulations such that flow in complicated geometries can be studied. It is also worth pointing out that the lattice Boltzmann methods ideally lend themselves to parallelization. A snapshot of a complex sound generating air flow in a recorder calculated with the lattice Boltzmann method is shown in Figure 7.

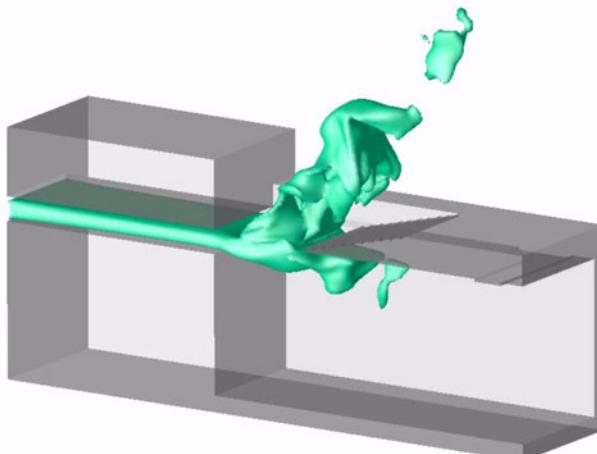


Figure 7. Complex air flow in a recorder as computed with the lattice Boltzmann method. Shown in green is an iso-speed surface at 40% of the maximum jet speed (simulation and figure by Helmut Kühnelt, University of Vienna).

The lattice Boltzmann method is more intimately related to the Boltzmann equation than suggested by its historic origin from lattice gas cellular automata. In fact, the lattice Boltzmann method, or, more properly, the lattice Boltzmann equation, can be directly derived from the Boltzmann equation in the relaxation approximation of Bhatnagar, Gross and Krook [109]. In this approximation, also a direct numerical solution of the Boltzmann equation with finite differences is possible. However, the computational effort is extremely challenging particularly for turbulent flow.

## 9 Coda

It is an amazing fact that even 100 years after Boltzmann scores of scientists have not been able to come to the bottom of many of the problems he so boldly sketched for us. This testifies to the inherent difficulties related to these problems, but also to the incredible creativity and insight from Boltzmann's part to recognize and isolate the essence of many problems and to provide a mathematical framework which has withstood the test of time. Although he could not foresee the possibilities computers offer to the present-day statistical physicist, his logic has very often been translated into computer algorithms capable of illuminating some aspects of the interplay between the

microscopic and macroscopic world. He is still considered the patron saint of their craft by most computational statistical physicists.

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c) Mensch. Unter den deformirbaren Körpern ist einer, der seine Deformationen mit Bewusstsein erzeugen kann. Das ist der Mensch. Indem er einen Körper  $A$  vorübergehend an sich befestigt, kann er ihn entweder deformiren oder beschleunigen. Bewegungswirkungen, die wir ausüben, sind für uns mit einem gewissen Anstrengungsgefühl verknüpft; der augenblickliche Betrag desselben ist für uns roh schätzbar; wenn wir z. B. das eine Mal an einem Cubikcentimeter, das andere Mal an einem Cubikdecimeter massiven Eisens eine bestimmte Beschleunigung anbringen, so ist der Unter-

Budde, Mechanik. I.

8

*Seinen Körper mit Bewusstsein deformatieren, kann nur der Mensch – aber solchen Stiefel schreiben, kann allerdings nur das Schwein.*

Ironical comment by Ludwig Boltzmann in E. Budde's textbook on mechanics  
("Seinen Körper mit Bewusstsein deformieren, kann auch das Schwein –  
aber solchen Stiefel schreiben, kann allerdings nur der Mensch")

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# Statistical properties of the cluster dynamics of the systems of statistical mechanics

A. Gabrielov, V. Keilis-Borok, Ya. Sinai, and I. Zaliapin

## Introduction

L. Boltzmann was the first who tried to explain the laws of thermodynamics and kinetics as corollaries of dynamics of large systems of interacting particles (see his classical book [1]). In particular, Boltzmann derived the classical Boltzmann kinetic equation based on his Stoßzahlansatz that gave the first “dynamical” explanation of irreversibility. The Stoßzahlansatz can be applied to any system of statistical mechanics which can be considered as a small perturbation of an ideal gas and undergoes the so-called Boltzmann-Grad limit transition (see [3]) when the length of the free path is of the order of the size of the whole system. O. Lanford (see [3]) gave the first mathematical proof of the local existence theorem of solutions of the Boltzmann equation where he showed convergence of correlation functions to solutions of the Boltzmann equation.

There were many attempts to extend the conditions under which the Boltzmann kinetic equation or its generalization works. In this connection we would like to mention the book by Bogolyubov [2] where Bogolyubov stressed several times the idea that in the gaseous phase when the interaction between the particles is short-ranged the system can be decomposed into finite clusters so that during some random interval of time each cluster moves independently of other clusters as a finite-dimensional dynamical system. After such random time the system can be decomposed again into other dynamically independent clusters and so on. It is natural to call this type of dynamics *cluster dynamics*.

The cluster dynamics was shown to exist in one-dimensional systems of statistical mechanics in [4]. Consider the infinite system of one-dimensional particles with pairwise interaction having a hard core and short range. Assume that the distribution of particles is given by the Gibbs canonical distribution. In the one-dimensional case in the thermodynamical limit there is no difference between canonical and grand canonical distributions. According to these distributions in a typical situation on any interval  $[-R, R]$  there are empty intervals of the length  $O(\ln R)$  having at  $t = 0$  no particles. On the other hand, the velocities of the particles have the Gaussian distribution. Therefore for any  $T$  the velocities of the particles on  $[-R, R]$  grow typically as  $O(\sqrt{\ln R})$ . It shows that for sufficiently large  $R$  particles cannot go from one end-point of an empty interval to the other one. In other words for any  $T$  in the finite-dimensional dynamics particles in the domains bounded by empty intervals do not interact with external particles. This gives cluster dynamics. The accurate proof requires some probabilistic estimates which show that the velocities do not become large during the finite-dimensional dynamics (see [4]). All these ideas were generalized to the multi-dimensional case and low density, *i.e.* to the gaseous phase in [5].

The infinite system of equations of motion of particles  $(x_i, v_i)$  of mass  $m = 1$  has the form

$$\frac{dx_i}{dt} = v_i, \quad \frac{dv_i}{dt} = - \sum_j \frac{\partial U(|q_i(t) - q_j(t)|)}{\partial q_i} \quad (1)$$

In the paper by E. Presutti, M. Pulvirenti and B. Tirozzi [6] the authors proved the general existence theorem for solutions of (1) for any limit Gibbs distribution with arbitrary density and inverse temperature. Their method is based upon the reduction of (1) to the corresponding integral equation and the proof of existence of solutions of the integral equation.

The most general results were obtained by R. Dobrushin and J. Fritz (see [7]). They described a large subset in the phase space of (1) for which they proved 1) the existence theorem of solutions and 2) the fact that the probability of this subset with respect to any natural Gibbs distribution is 1. This gives the possibility to describe the dynamics in the space of Gibbs distributions.

Recently, it turned out that the concept of cluster dynamics has a wider domain of applications in such fields as plasma physics, geophysics and others (see, for example, [20], [21]). In this connection it is interesting to study the distributions of various characteristics of cluster dynamics, such as the distribution of the size of the clusters, the statistics of particles in a cluster and others. The whole set of problems resembles problems of percolation theory but seems to be more difficult than the percolation theory because it involves dynamical characteristics. There is no hope that something can be done analytically. On the other hand, the use of computers opens wide possibilities in getting numerical results. The corresponding experiments were performed recently and the results are presented below in this paper. We want to stress the appearance of new critical indices which are special for cluster dynamics and presumably are different from similar ones in percolation theory.

In this paper we analyze numerically cluster dynamics in a simplest system – a frictionless elastic billiard. The model and cluster rules are described in Section 1. We report a phase transition in the cluster formation process in Section 2 and describe how it depends on the model parameters in Section 3. Also, we study how the size of the maximal cluster in a finite system scales with the system size (Section 4). Section 5 describes possible applications of cluster dynamics. Details of our numerical simulations are given in Section 6.

## 1 Model

The results in this paper refer to an elastic frictionless billiard on a square table. Namely, we consider  $N$  balls of mass  $m = 1$  and radius  $R$  placed within the region  $\mathcal{T} = \{(x, y) : |x| \leq L/2, |y| \leq L/2\}$ . We will call  $N$  the size of the billiard. Each ball moves without friction with constant velocity  $\mathbf{v}_i = (v_x^i, v_y^i)$ ,  $i = 1, \dots, N$  until it collides with a wall or another ball. All collisions are elastic, which means that the total energy  $E = \sum_{i=1}^N m |\mathbf{v}_i|^2 / 2$ ,  $|\mathbf{v}_i|^2 = (v_x^i)^2 + (v_y^i)^2$ , of the system remains constant, the total momentum  $\mathbf{p} = \sum_{i=1}^N m \mathbf{v}_i$  is not affected by ball collisions, and in wall collisions

the ball's reflection and incidence angles are the same. A useful characteristic of the billiard is the density of balls:

$$\rho = \frac{N \pi R^2}{L^2}. \quad (2)$$

We will need the notion of  $\Delta$ -cluster [4], which is a group of balls that have affected each others dynamics during the time interval of duration  $\Delta$ . Formally, we call two balls  $\Delta$ -neighbors at epoch  $t$  if they collided during the time interval  $[t - \Delta, t]$ . Any connected component of this neighbour relation is called a  $\Delta$ -cluster at epoch  $t$ . This definition ensures that each ball has collided with at least one ball from its  $\Delta$ -cluster within the time interval  $[t - \Delta, t]$ . The mass of a cluster is the total mass of its balls. We denote by  $N_\Delta(t)$  the total number of  $\Delta$ -clusters at instant  $t$ , and by  $M_\Delta^i(t)$  the mass of the  $i$ -th largest cluster. Thus, the mass of the maximal  $\Delta$ -cluster is  $M_\Delta^1(t)$ , of the second largest cluster  $M_\Delta^2(t)$ , of the smallest cluster  $M_\Delta^{N_\Delta}(t)$ , etc.

Obviously, at  $\Delta = 0$  there exist  $N$  clusters of mass  $m$ , each corresponding to an individual ball. As  $\Delta$  increases, the balls start to collide so the number of clusters becomes smaller while their masses increase. In this note we only consider a situation when  $\Delta = t$ , that is we deal with all the clusters that have been formed during the time interval  $[0, \Delta]$ . This allows us to drop the dependence on  $t$  and work with the number of clusters  $N_\Delta$ , maximal cluster of mass  $M_\Delta^1$ , etc.

In this paper we focus on the time-dependent distribution (density)  $f_t(M)$  of cluster sizes (masses). In a numerical study, to obtain a sample of  $n$  clusters at epoch  $t$  one runs the model  $n$  times, each time choosing a single cluster at epoch  $t$ . A standard practice in stochastic geometry suggests to choose the cluster nearest to the origin (that is the cluster that contains the ball nearest to the origin). It happens that the computational load associated with this procedure is prohibitive for our purposes. To make the computations workable, we approximate the cluster size distribution  $f_t(M)$  using the entire cluster population from a single realization of the model, which has density  $g_t(M)$ . For large  $N$ ,  $f_t(M)$  becomes an *area-biased* version of  $g_t(M)$ , since large clusters have a better chance to lie closer to the origin than smaller ones; and the two distributions are connected via [11]:

$$f_t(M) = \frac{M g_t(M)}{\int M g_t(M) dM}. \quad (3)$$

The results in this paper refer to  $g_t(M)$ .

## 2 Phase transition in dynamical clustering

To study the dynamics of clusters we have considered models with  $10^{-8} \leq \rho \leq 10^{-1}$ , and  $1 \leq N \leq 10^4$ . We run each model until the instant when a cluster of mass  $0.95 \times N$  is formed.

Figure 1 shows fractional masses  $\mu_\Delta^i = M_\Delta^i/N$  of clusters as a function of time when they have been formed; this figure refers to  $\rho = 10^{-3}$ ,  $N = 10^4$ . Here we see the following generic qualitative picture that has been observed for *all* the models

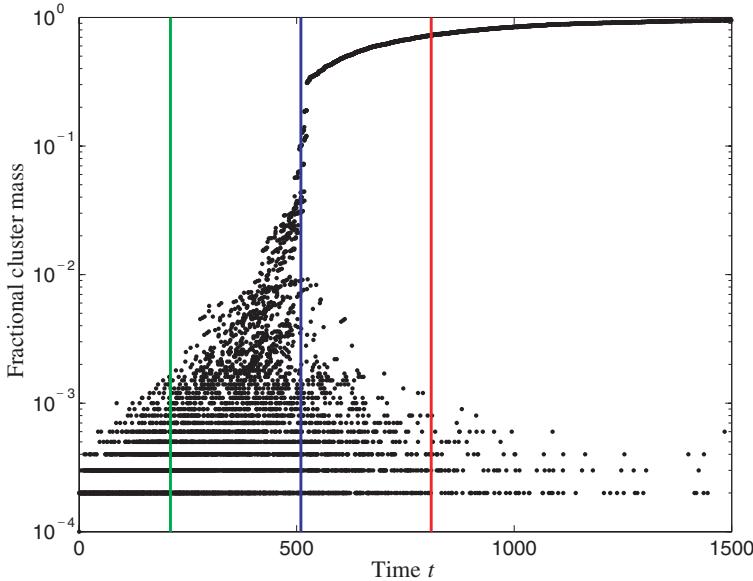


Figure 1. Fractional cluster masses  $\mu_{\Delta}^i = M_{\Delta}^i/N$  as a function of time when they have been formed in a model with  $\rho = 10^{-3}$ ,  $N = 10^4$ . Each point corresponds to a single cluster. The horizontal lines at the lower part of the figure are formed by a multitude of clusters of mass  $M = 2$  (lowest line),  $M = 3$  (second line), etc. The point  $(0, 10^{-4})$  refers to  $N = 10^4$  balls, each of which forms a cluster of unit mass at  $t = 0$ . Notice the dramatic change in the cluster mass distribution at the moment  $t_c \approx 510$  depicted by blue vertical line. Three vertical lines correspond to the three cluster size distributions in Figure 2.

considered. At  $\Delta = 0$ , we start with  $N$  clusters of mass  $m$ . As the model evolves, clusters of increasingly larger masses are formed and the total number of clusters decreases. For some period of time,  $0 \leq t \leq t_c$  (for this model,  $t_c \approx 510$ ) the cluster mass distribution has no notable gaps, in particular the size of the largest cluster does not exceed significantly the size of the second largest cluster. At  $t = t_c$  one observes a sharp qualitative change in the cluster formation process. There appears a distinctive largest cluster, which creates a gap in the mass distribution between the largest cluster and the rest of the clusters. Notably, this change happens when the largest cluster is still relatively small: less than 10% of the total system mass.

It will be convenient to define formally the time instant  $t_c$  that corresponds to the change in cluster formation. We define here  $t_c$  as the instant after which there are no clusters larger than  $M_{t_c}^1$ :

$$t_c = \inf\{t : M_t^1 > M_s^i, s > t, i > 1\}. \quad (4)$$

We will refer to  $t_c$  as *critical time*. Note that this definition uses the information from the times  $t > t_c$  (*i.e.*,  $t_c$  is not a stopping time), so it cannot be used for operational detection of  $t_c$ . It would be useful to have an alternative definition which will use only

the information available prior  $t_c$ .

Figure 2 shows the empirical cluster mass density for the model with  $\rho = 10^{-3}$  and  $N = 10^4$  at three time instants depicted by vertical lines in Figure 1.

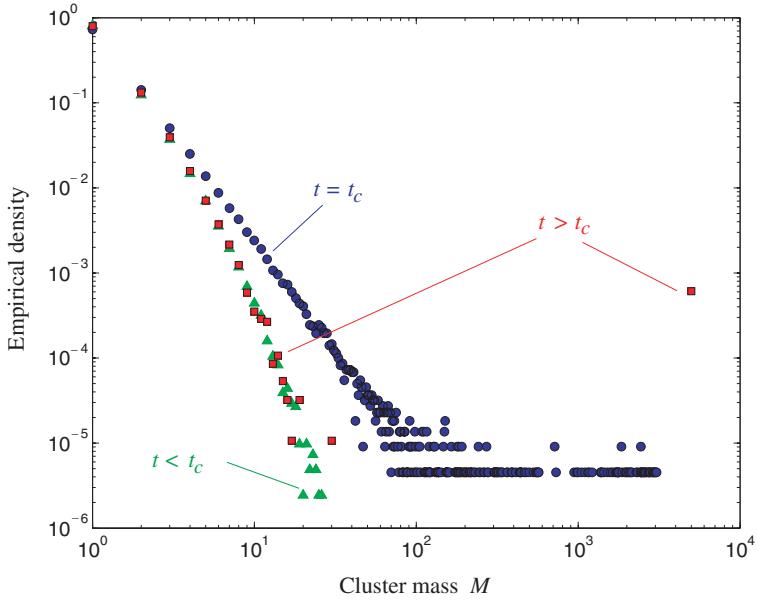


Figure 2. Cluster size distribution at three instants depicted by vertical lines in Figure 1. At  $t < t_c$  (green triangles) distribution can be approximated by a power law with exponential taper at the tail; at  $t \approx t_c$  (blue balls) it is a pure power law; at  $t > t_c$  (red squares) it is a tapered power law plus a  $\delta$  function at the largest cluster. To produce this figure we used 50 independent realizations of the model with  $\rho = 10^{-3}$ ,  $N = 10^4$ .

For  $t \leq t_c$  the cluster mass distribution  $g_t(M)$  is well described by a power law with an exponential taper:

$$g_t(M) = M^{-\beta} \exp\left(-\frac{M}{\gamma(t)}\right). \quad (5)$$

Here  $\beta \approx 5/2$ , and the taper strength is determined by  $\gamma(t)$ :  $\gamma(t) \ll M$  leads to almost an exponential distribution, while  $\gamma(t) \gg M$  to a pure power law. Our simulations suggest that  $\gamma(t)$  is monotone increasing with  $\gamma(t_c) = \infty$ , so that  $g_t(M)$  transforms from exponential at small times  $t \ll t_c$  to a pure power law at the critical epoch  $t_c$ . One can readily see the scenario that characterizes systems with phase transition of second kind. In statistical mechanics, equation (5) describes the correlation function  $\Gamma(r)$  of a system (*e.g.*, Potts model) near the critical point. A similar power law with exponential taper was suggested for the mass distribution of clusters in a percolation model [12], [13] as the percolation instant approaches; for rupture sizes in a colliding cascades model of earthquakes [14], [15], [17]; for real ruptures in steel samples [16],

etc. For  $t > t_c$  the distribution is decomposed into two components: A  $\delta$ -function at the mass of the largest cluster, and the tapered power law (5) for the rest of the clusters with  $\gamma(t)$  monotone decreasing for  $t > t_c$ .

This picture is observed for all the models considered independently of the billiard density  $\rho$  and size  $N$ . In particular, the critical index  $\beta \approx 5/2$  is universal: Figure 3 show the cluster mass distribution at  $t_c$  for seven different models with  $N = 5 \times 10^3$  and  $\rho = 10^{-1}, 10^{-2}, \dots, 10^{-7}$ .

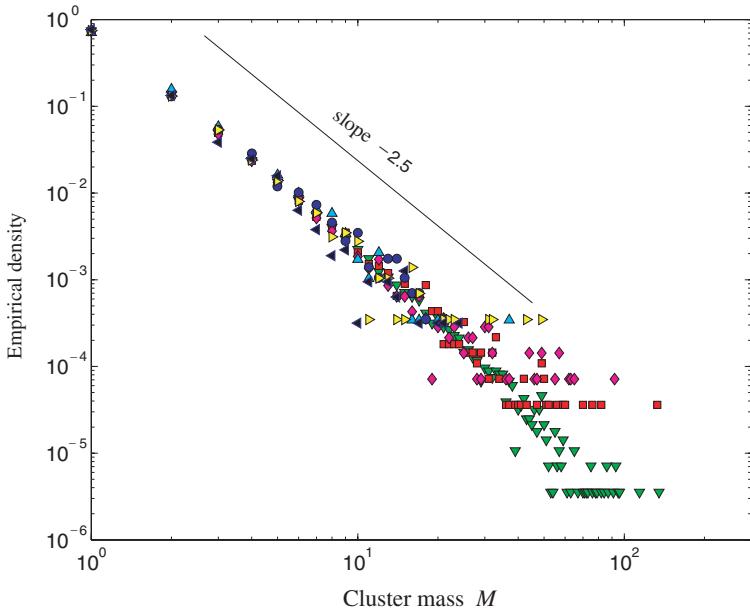


Figure 3. Power-law cluster size distribution at critical instant  $t_c$  for seven models with fixed  $N = 5 \times 10^3$  and  $\rho = 10^{-1}, 10^{-2}, \dots, 10^{-7}$ . The distribution at critical instant  $t_c$  is characterized by a universal index  $\beta = 5/2$ .

### 3 Scaling of critical time and mass

Here we study how the critical instant  $t_c$  and the fractional mass  $\mu_c := M_{t_c}^1/N$  of the largest cluster at  $t_c$  depend on the billiard density  $\rho$ . For that we run multiple (from 10 to 1000) realizations of the billiard for  $\rho = 10^{-1}, 10^{-2}, \dots, 10^{-7}$  and  $N = 5 \times 10^3$ . The averaged values of  $t_c$  and  $\mu_c$  are shown in Figures 4, 5 as functions of  $\rho$ . These results support the following asymptotic relations, which give very good approximation for  $\rho < 10^{-2}$ :

$$t_c(\rho | N = 5 \times 10^3) \approx 0.4 \rho^{-1}, \quad \mu_c(\rho | N = 5 \times 10^3) \approx 0.07, \quad \text{as } \rho \rightarrow 0. \quad (6)$$

A more detailed analysis (not shown) indicates that the large density correction for critical time is given by:

$$t_c(\rho | N = 5 \times 10^3) = 0.4 \rho^{-1} (1 + \rho^{0.4} + o(\rho^{0.4})) , \quad \rho \rightarrow 0. \quad (7)$$

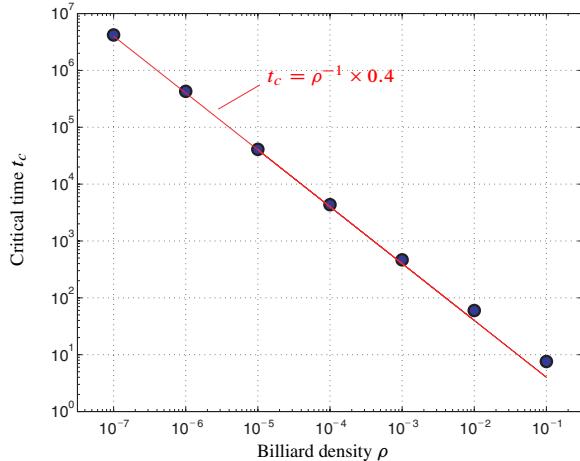


Figure 4. Scaling of critical time  $t_c$  with the billiard density  $\rho$  at fixed  $N = 5 \times 10^3$ .

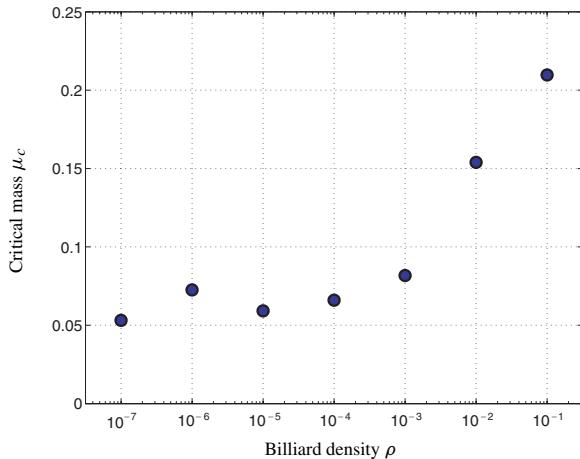


Figure 5. Critical mass  $\mu_c$  as a function of the billiard density  $\rho$  at fixed  $N = 5 \times 10^3$ .

## 4 Size of the maximal cluster

Here we consider the dynamics and scaling of the maximal cluster. Figure 6 shows the dynamics of the fractional mass  $\mu_{\Delta}^1 = M_{\Delta}^1/N$  of the largest cluster averaged over 10 to 1000 realizations of a billiard; it refers to ten models with  $10 \leq N \leq 10^4$  and fixed

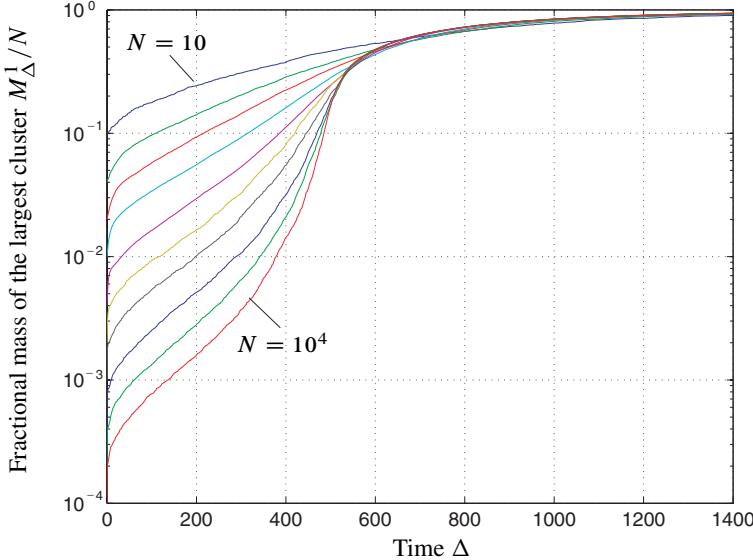


Figure 6. Fractional mass  $\mu_{\Delta}^1 = M_{\Delta}^1/N$  of the maximal cluster as a function of  $\Delta$  for ten models with fixed  $\rho = 10^{-3}$  and  $10 \leq N \leq 10^4$  (each line corresponds to a distinct value of  $N$ ).

$\rho = 10^{-3}$ . By construction, we have the following limiting relations:

$$M_0^1 = 1, \quad M_{\infty}^1 = N. \quad (8)$$

Next we study in detail the scaling of  $M_{\Delta}^1$  as a function of  $N$  and  $\Delta$ . Figure 7 shows  $M_{\Delta}^1$  as a function of  $N$  at eight time instants between  $\Delta = 0$  and  $\Delta = 1400 \approx 3 \times t_c$ . One can see a gradual transition between the limiting scalings (8). Approximately linear form of the plots suggests that we have a power law dependence

$$M_{\Delta}^1 = c(\Delta) N^{\alpha(\Delta)}, \quad (9)$$

with  $c(0) = c(\infty) = 1$ ,  $\alpha(0) = 0$ , and  $\alpha(\infty) = 1$ . Maximum likelihood estimations of  $c(\Delta)$  and  $\alpha(\Delta)$  for  $0 \leq \Delta \leq 1400$  are shown in Figure 8. At critical time we have  $\alpha(t_c) \approx 2/3$ .

A more detailed analysis (not shown) indicates that at initial times ( $0 < t < t_c/3$ ) the maximal cluster size in a finite system of size  $N$  is proportional to  $\log_{10} N$ :

$$M_{\Delta}^1 = \alpha'(\Delta) \log_{10}(N) + c'(\Delta). \quad (10)$$

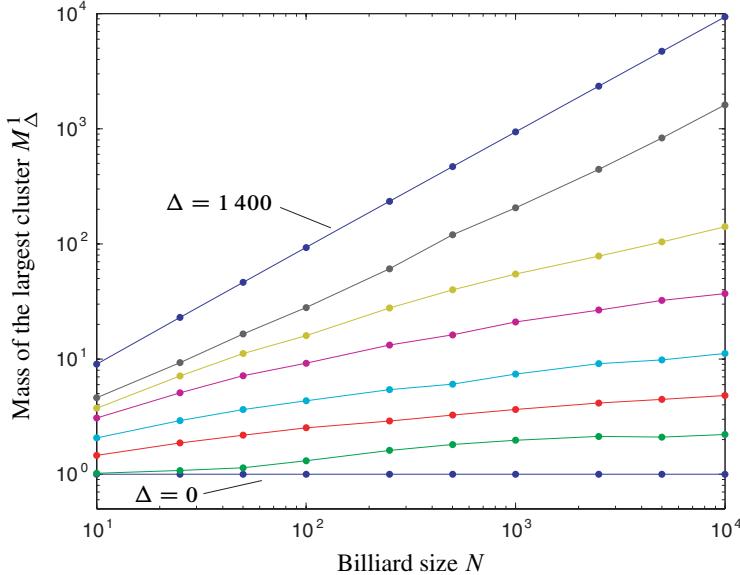


Figure 7. Mass  $M_{\Delta}^1$  of the maximal cluster as a function of billiard size  $N$  – each line corresponds to a distinct value of  $\Delta$ . Experiment is done under fixed  $\rho = 10^{-3}$ .

There exists a natural connection between this transition from logarithmic to power scaling of the maximal cluster size and from exponential to power tail of the cluster size distribution (see equation (5) and Figure 2). Indeed, suppose that cluster sizes are independent and identically distributed with distribution function  $F(x)$  and density  $f(x)$ . Then the size of the maximal among  $N$  clusters has distribution  $F_{\max}(M) = F^N(M)$  and density  $f_{\max}(M) = N f F^{N-1}$ ; and the most probable size  $M^*$  of the maximal cluster is given by the finite solution of  $\frac{d}{dM} f_{\max}(M^*) = 0$ . It is readily verified that

$$F(M) = 1 - e^{-\lambda M} \Rightarrow M^* = \frac{\ln(N)}{\lambda} \propto \ln(N), \quad (11)$$

$$F(M) = 1 - M^{-b} \Rightarrow M^* = \left( \frac{N b + 1}{b + 1} \right)^{1/b} \propto N^{1/b} + o(N^{1/b}). \quad (12)$$

The exponential tail of the cluster size distribution at  $t < t_c$  thus justifies the logarithmic dependence (10) of the maximal cluster size on  $N$ ; while the power law cluster size distribution around  $t_c$  explains the power law scaling (9). Equations (9) and (12) suggest  $b = 1/\alpha$ . We notice that the index  $b = \beta - 1 \approx 3/2$  of the cluster size distribution observed at  $t_c$  (see Figure 3) is indeed equal to  $1/\alpha \approx 1/0.66 \approx 3/2$  observed at  $t_c \approx 510$  in the top panel of Figure 8.

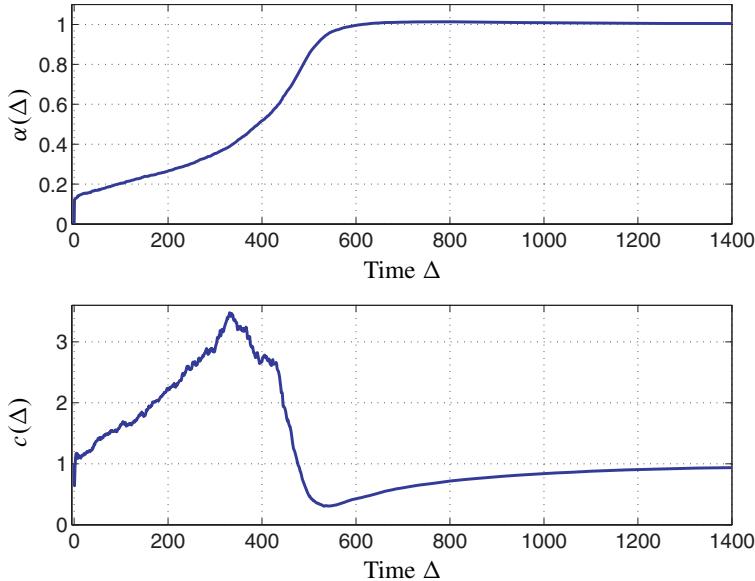


Figure 8. Parameters  $\alpha$  and  $c$  of scaling law (9) as functions of time  $\Delta$ . Each line in Figure 7 corresponds to one point in each panel of this figure. To produce this figure we used models with fixed  $\rho = 10^{-3}$ , and  $10 \leq N \leq 10^4$ .

## 5 Possible applications of cluster dynamics

We have demonstrated in Section 2 (Figures 1, 2) above that the distribution of the cluster size in the elastic frictionless billiard changes as the phase transition approaches. A similar phenomenon has been observed in seismicity and economics, where it is related to the approach of an appropriately defined critical event. Below we briefly discuss cluster dynamics in seismicity. More detailed discussion and further examples, suggesting universality of that phenomenon, are given in [19], [20], [21].

**Seismicity.** An earthquake is an episode of rupture and discontinuous displacement in the outer shell of solid Earth, called the lithosphere. Generally speaking, nucleation of a single earthquake is controlled by the clash between stress- and strength-fields in its vicinity. Both these fields, particularly the strength, are in turn controlled by a multitude of processes generating strong instability. Among them are interactions with other earthquakes, mechanical and chemical interactions of rocks and fluids, phase transitions of minerals, heat flow, non-linear deformations and fracturing, interactions between geospheres, incompatibility between the structure and kinematics, *etc*. These processes evolve in multiple scales, from global to microscopic ones. Altogether they turn the lithosphere into a hierarchical dissipative non-linear (“complex”) system. Fundamental equations connecting seismicity with this set of intertwined mechanisms are not yet known.

**Scale invariance.** Size of an earthquake is usually defined as its magnitude  $m$  – a logarithmic measure of the energy  $E$  released by the earthquake [8] ( $m = 2/3 \log_{10} E + C$ ). About  $10^6$  earthquakes with  $m > 2$  are recorded annually worldwide, and once in a few years the largest earthquakes with  $m > 8$  occur. The magnitude distribution of earthquakes is known in seismology as the Gutenberg–Richter law [9], [10]:

$$\log_{10}(N(m)) = a - bm. \quad (13)$$

Here  $N(m)$  is the average annual number of earthquakes with magnitude  $m$  or more,  $b \approx 1$ . The Gutenberg–Richter law emerges only after considerable averaging of seismicity over time and territory and gives a good description for small to medium magnitudes. At the relatively large magnitudes, the size distribution bends downwards. The linear relation (13) is equivalent to the power law distribution of earthquake energy:

$$N(E) \propto E^{-\beta}, \quad \beta \approx 2/3. \quad (14)$$

To accommodate the downward slope of the energy distribution at larger magnitudes, it can be approximated by an exponentially tapered distribution:

$$N(E) \propto E^{-\beta} \exp(-E/E_0). \quad (15)$$

Strong earthquakes are usually defined as outliers in observed distributions – “extreme events”. Such earthquakes are associated with abrupt overall changes of seismicity, and, qualitatively, with phase transitions.

**Clustering and phase transitions.** Earthquakes come in a hierarchy of clusters formed in a broad range of time-, space-, and magnitude scales, from microscopic to global ones. Clusters emerge, coalesce, split, migrate, and alternate with seismic quiescence (“anti-clusters”). As a strong earthquake approaches, distribution of cluster sizes tends to change in favor of larger clusters. Similarly, the magnitude distribution of individual earthquakes changes in favor of larger magnitudes. In particular, the distribution (15) changes similarly to the cluster size distribution (5) described in Section 2. These phenomena have been found in real seismicity of numerous regions worldwide as well as in numerical models of seismicity. They were used in several earthquake prediction algorithms, self-adjusting to statistical properties of seismicity in different regions [21]. Statistical significance of predictions based on that kind of clusters is demonstrated in [23].

Similar changes in scaling relations have been observed before American economic recessions and some socio-economic extreme events [20].

## 6 Parameters and simulation details

We have simulated the billiard for  $1 \leq N \leq 10^4$  and  $10^{-8} \leq \rho \leq 1/2$ . The table size  $L$  was kept constant, while appropriate values of  $R$  for any given  $\rho$  and  $N$  were calculated via (2). We put  $m = 1$  and  $T = 1/k_B$ .

Recall that the Maxwellian velocity distribution of an ideal gas in  $D$ -dimensional space is given by

$$f(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{D/2} \exp^{-m|\mathbf{v}|^2/(2k_B T)}, \quad (16)$$

where  $\mathbf{v} = (v_1, \dots, v_D)$ ,  $|\mathbf{v}|^2 = v_1^2 + \dots + v_D^2$ ,  $k_B$  is Boltzmann constant,  $T$  temperature, and  $m$  particle mass. Accordingly, the speed  $s := |\mathbf{v}|$  of particles in a  $2D$  system is given by Chi-distribution with two degrees of freedom:

$$p(s) = s \sqrt{\frac{m}{k_B T}} \exp^{-ms^2/(2k_B T)}. \quad (17)$$

We have verified that any (non-degenerate) initial velocity distribution eventually transforms to the Maxwellian distribution (16). The rate of convergence is rather fast; say, the isotropic uniform initial velocity distribution for  $N = 500$  balls transforms into the Maxwellian distribution after 2 000 ball collisions, which is 4 collisions per ball on average.

We start all our models with the Maxwellian velocity distribution (16) and uniform placement of the balls. Specifically, the balls are placed on the table one-by-one. The center of the first ball is uniformly distributed within the region

$$\mathcal{T}' = \{(x, y) : |x| < L/2 - R, |y| < L/2 - R\},$$

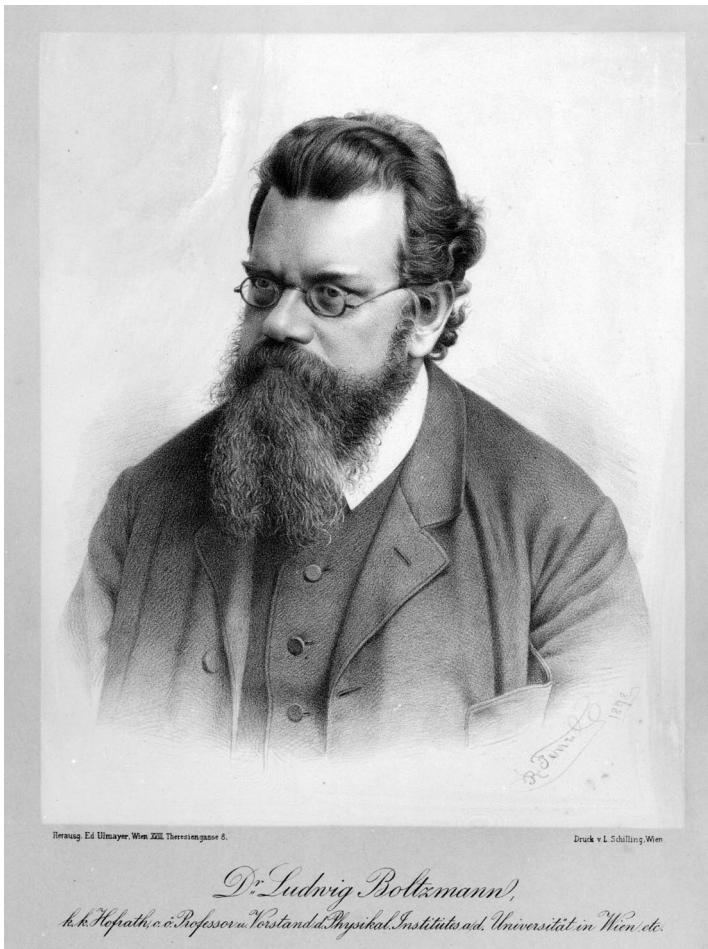
which ensures that it does not intersect with the table walls. The center of  $(k+1)$ -th ball,  $k \geq 1$ , is uniformly distributed within the region  $\mathcal{T}' \setminus B_k$ , where  $B_k$  is the union of already placed balls; this ensures the new ball does not intersect with existing balls and the walls.

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*Dr. Ludwig Boltzmann,  
k.k. Hofpath. u. c. Professor u. Vorstand d. Physikal. Instituts ad. Universität in Wien, etc.*

Ludwig Boltzmann in Vienna 1902  
(Courtesy of Ilse M. Fasol-Boltzmann and Gerhard Ludwig Fasol)

# Boltzmann and evolution: some basic questions of biology seen with atomistic glasses

Peter Schuster\*

## 1 Boltzmann and biology

In his popular lecture on the second law of thermodynamics Ludwig Boltzmann made two highly remarkable statements about evolution and biology.<sup>1</sup> The first is dealing with the role of Charles Darwin and his theory of evolution [7, p. 29]:

... Wenn Sie mich nach meiner innersten Überzeugung fragen ob man unser (das 19.) Jahrhundert einmal das eiserne Jahrhundert oder das Jahrhundert des Dampfes oder der Elektrizität nennen wird, so antworte ich ohne Bedenken, das Jahrhundert der mechanischen Naturauffassung, das Jahrhundert Darwins wird es heißen. ...

... If you ask me about my innermost conviction whether our century will be called the century of iron or the century of steam or electricity, I answer without hesitation: It will be called the century of the mechanical view of Nature, the century of Darwin. ...

In order to interpret this sentence properly in our current terminology *mechanical* should be replaced *mechanistic*. Boltzmann went even further in his thoughts and made clear statements that indicate the beginning of an evolutionary theory of cognition. The second statement deals with energy, entropy and photosynthesis and is even more remarkable, because it anticipates the molecular view of present day biology [7, p. 41]:

... Der allgemeine Daseinskampf der Lebewesen ist daher nicht ein Kampf um die Grundstoffe – die Grundstoffe aller Organismen sind in Luft, Wasser und Erdboden im Überflusse vorhanden – auch nicht um Energie, welche in Form von Wärme leider unverwandelbar in jedem Körper reichlich vorhanden ist, sondern ein Kampf um die Entropie, welche durch den Übergang der Energie von der heißen Sonne zur kalten Erde disponibel wird. Diesen Übergang möglichst auszunutzen, breiten die Pflanzen die unermeßliche Fläche ihrer Blätter aus und zwingen die Sonnenenergie in noch unerforschter Weise, ehe sie auf das Temperaturniveau der Erdoberfläche herabsinkt, chemische Synthesen auszuführen, von denen man in unseren Laboratorien noch keine Ahnung hat. Die Produkte dieser chemischen Küche bilden das Kampfobjekt für die Tierwelt. ...

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\*Part of this article has been written at the Santa Fe Institute within the External Faculty Program.

<sup>1</sup>Ludwig Boltzmann, *Der zweite Hauptsatz der mechanischen Wärmetheorie*. Lecture presented at the 'Festive Session' of the Imperial Academy of Sciences in Vienna, May 29, 1886. The German text is taken from [7] and the English translation from [8].

... The general struggle for existence of living beings is therefore not a fight for the elements – the elements of all organisms are available in abundance in air, water, and soil – nor for energy, which is plentiful in the form if heat, unfortunately untransformably, in every body. Rather it is a struggle for entropy that becomes available through the flow of energy from the hot Sun to the cold Earth. To make the fullest use of this energy, the plants spread out the immeasurable areas of their leaves and harness the Sun's energy by a process that is still unexplored, before it sinks down to the temperature level of the Earth, to drive chemical syntheses of which one has no inkling as yet in our laboratories. The products of this chemical kitchen are the object of the struggle ion the animal world. ...

'Entropy' in Boltzmann's lecture should presumably be replaced here by 'Negentropy' as it has been used by Erwin Schrödinger in his famous lectures on 'What is life' in Dublin [55]:

... What an organism feeds upon is negative entropy. Or to put it less paradoxically, the essential thing in metabolism is that the organism succeeds in freeing itself from all the entropy it cannot help producing while alive. ...

The recognition of negentropy, or more correctly free energy, as the object at stake in the struggle for existence and in the evolution of life was not a privilege of physicists. The famous biologist and mathematician D'Arcy Thompson gives a very clear account on the energetic basis of life in his book 'On Growth and Form' [66] that was published first in 1917. Although Boltzmann's statement about the – for life on Earth for practical reasons – unlimited availability of mineral components is true under most circumstances, limitations of growth because of shortage in phosphorous have been reported and are well documented for more than seventy years [53], [14], [68]. The essential components of biomass production as we know them nowadays are indeed sunlight and water. It is interesting that liquid water is addressed as a *conditio sine qua non* rather rarely by the scholars of physics.

Charles Darwin's theory of evolution [10] can be casted in five statements [38, p. 34]:

- (i) Evolution is a real historic process. Species are subject to change and have evolved over millions of years from precursor species.
- (ii) The driving force for the evolution of species is the interplay of variation and selection in populations.
- (iii) All living beings descend from a common ancestor that represents the root of the *tree of life*.
- (iv) Phylogeny proceeds gradually and not stepwise.
- (v) Precursor species are split into daughter species during phylogeny and lead thereby to branches in the tree of life.

Evidence for all five concepts has been found in Nature. There is an exception of statement (iv), because punctuation in the appearance of species seems to occur as

well. Statements number (i), (iii), and (v) form the conventional view of biological evolution giving rise to the tree of life. A slight modification is necessary in the light of horizontal gene transfer.<sup>2</sup> Statement (ii) provides the mechanism of optimization in the Darwinian scenario: Multiplication of organisms leads to more progeny than the numbers of individuals that can be sustained by the ecosystem. As an highly relevant side effect it produces a distribution of variants by unperfect coping and recombination.<sup>3</sup> Variation and selection of the fittest in the sense of maximum number of progeny leads, inevitably, to an optimization of the number of fertile offspring. In Section 4 we shall present and discuss mathematical models, in Section 5 computer simulation of optimization through variation and selection.

Boltzmann's pleading for evolution as the key to understand biology and the world was precisely to the point. It was formulated almost ninety years later by Theodosius Dobzhansky, one of the scholars of the synthetic theory of evolution. He said the famous sentence [13]:<sup>4</sup>

'Nothing in biology makes sense except in the light of evolution'.

Another interesting detail concerns atomism or discreteness and biological evolution. Charles Darwin and the selectionists of the first half of the twentieth century thought that evolution proceeds in small steps (statement iv). They were influenced by the dominant view of geologists in the nineteenth century who believed in gradualism [54], [42], [38]. Large numbers of small changes shape the evolutionary process. Gregor Mendel's discoveries of the laws of inheritance introduced discreteness into evolutionary theory. As a matter of fact Mendel had introduced 'atoms of inheritance' – nowadays called genes – into biology. Would it not have been natural for Ludwig Boltzmann to join the party of the geneticists rather than the selectionists? Although Mendel's work stayed almost unnoticed during the second half of the nineteenth century, it was rediscovered around the turn of the century and Boltzmann could well have been aware of it.<sup>5</sup>

An even more important concept that influenced further development of evolutionary biology was August Weismann's hypothesis on the strict separation of the potentially immortal cells of the germline, which can be transferred to children, and the somatic cells, which die at the latest together with their carrier organism [70], [67]. Together with Darwin's natural selection and Mendel's rules of inheritance the germline hypothesis – now fully confirmed by cellular and molecular biology – builds the basis of the so-called Neodarwinian theory of evolution. An interesting historical detail concerns Charles Darwin's thoughts about inheritance: All his life and even more outspoken in the later issues of the 'Origin of Species' Darwin believed in the transmission of acquired

<sup>2</sup>Horizontal gene transfer is the exchange of genetic material between organisms living at the same time.

<sup>3</sup>Neither mutations nor recombination were known as sources of variation in Darwin's days. He himself believed in the hereditary acquisition of acquired capabilities as the source of variation. Thus, we would call him today a Lamarckian.

<sup>4</sup>The famous biologist and deep thinker of evolution Ernst Mayr gives an extensive account of the growth of biological thinking [42].

<sup>5</sup>Several biologists repeated and confirmed Gregor Mendel's breeding experiments. One of them, William Bateson [2] coined the term *genetics* and published a monograph that has become a classic on the origin of genetics.

properties to the progeny and considered it as the factor providing inheritable variation. In this sense Darwin was a Lamarckian. In the Neodarwinian theory inheritable modifications are only possible through changes of germ cells. Biology was split into two camps during the first decades of the twentieth century since selectionists and geneticists, as the distinguished biologist Wolfgang Freiherr von Buddenbrock-Hettersdorf said in 1930, were heavily fighting:

... The controversy ... is as undecided now as it was 70 years ago ... neither party had been able to refute the arguments of their opponents and one must assume that the situation is not going to change soon. ...

Fortunately, Buddenbrock's prediction did not become true. Already in the nineteen thirties a formal mathematical unification of Darwinian selection and Mendelian genetics was performed by the scholars of population genetics, Ronald Fisher, J. B. S. Haldane and Sewall Wright. Later, before and during World War II, the ultimate unification occurred in the synthetic theory of evolution that has been further extended by molecular life sciences [41], [52], [37].

## 2 Holism and reductionism

The holism versus reductionism debate is an old theme in philosophy and science. Sometimes holism is even traced back to Aristotle's Metaphysics that contains the famous sentence: "The whole is more than the sum of its parts". The problem here is the usage of the term *sum*. When sum implies a simple arithmetic sum, the statement expresses nothing more and nothing less than the parts of the whole do interact. For every property  $F(\Xi)$  of an ensemble  $\Xi = \{X_1, X_2, \dots, X_n\}$  we can write

$$F(\Xi) = \sum_{i \in \Xi} f^{(1)}(X_i) + \sum_{i \in \Xi} \sum_{j < i, j \in \Xi} f^{(2)}(X_i X_j) + \dots + f^{(n)}(X_1 \dots X_n) \quad (1)$$

The terms in the cluster expansion  $F(\cdot)$  corresponds to one body, two body and higher interaction contributions up to the  $n$  body term, for example

$$f^{(1)}(X_i) = F(X_i), \quad f^{(2)}(X_i X_j) = F(X_i X_j) - (F(X_i) + F(X_j)) \dots$$

In the naïve interpretation Aristotle's sentence then says that there are non-vanishing two or more body terms and therefore additivity is violated.

Apart from trivial non-additivity Aristotle's sentence has three deeper interpretations that can be casted into questions:

- (i) Are new properties emerging in the progression from a lower to a higher hierarchical level?
- (ii) Can we describe the phenomena on a higher hierarchical level by means of the laws operating on the lower level or do we need new laws of Nature that become operational in the form of specific forces only on the higher level?

- (iii) Are there limits in the predictability of complex systems that cannot be compensated by improved knowledge on the parts of the system?

The answer to question (i) will be almost always *yes*. We consider, for example, the world of atoms and the hierarchically higher world of molecules being composed of atoms. The chemical bond is part of the notions needed to describe the properties of molecules but does not exist in the world of atoms: The chemical bond is an emergent property.

Question (ii) asks whether the postulation of special laws and forces like the notorious vital force - *vis vitalis* - behind living organisms is indispensable. Additional forces causing essentially novel regularities on the higher level, which need new fundamental laws to describe them, are much harder to argue and to verify. In the life sciences this second version of holism has become very unpopular and the majority of scientists would currently agree that it is extremely unlikely to discover new fundamental forces in biology, psychology or sociology. In other words, there is a common belief that neither biology nor psychology nor sociology will lead to observations that contradict contemporary physics.<sup>6</sup>

Question (iii) addresses so-called scientific holism and finds its confirmation in the existence of principle reasons like quantum physical uncertainty or deterministic chaos and technical limitations, for example incomplete information on initial and boundary conditions.

Historically, the idea of reductionism has been introduced in the seventeenth century by René Descartes. He thought that the world was like a machine whose operations can be fully understood in terms of the mechanical parts like the operation of a mechanical clock can be explained if all its pieces and their relative positions are known. The most extreme form of reductionism is known as ontological reductionism and states that the ultimate explanation of everything has to be given in terms of most fundamental entities being elementary particles or strings. Daniel Dennett [12] calls this concept also "greedy reductionism". A milder form of reductionism is called hierarchical reductionism [11, p. 13]. It is related to the idea of a unity of science and states that complex systems can be described by a hierarchy of levels in which each form of organization is described in terms of the objects of the next lower level. Within science hierarchical reductionism is expressed, for example, by the statements: Fundamental chemistry is based on physics, fundamental biology is based on chemistry, psychology is based on biology, sociology is based on psychology and, eventually, political science, anthropology and economics are based on sociology. A majority of scientists is accepting the first two reductions, chemistry  $\Rightarrow$  physics and biology  $\Rightarrow$  chemistry, but at present the other reductions are strongly opposed by many researchers. Examples are the controversial discussions of the interpretations of observations from sociobiology or evolutionary psychology [9]. Methodological reductionism or the reductionists' program, on the other hand, is the method of handling problems in science if one aims at going beyond pure narrative descriptions. Physics is the discipline that has most

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<sup>6</sup>A related but more radically formulated view comparing bottom-up explanations with *deus ex machina* solutions is found under the heading 'Skyhooks or cranes?' in Daniel Dennett [12, p. 73].

experience with reduction but everywhere in science experimental exploration of regularities requires reduction in the sense of simplification and constant environments in particular in many variable systems. Even for understanding how and why the whole is more than the sum of its parts profound knowledge of the parts is indispensable. It seems useful to end the academic holism versus reductionism debate by referring to the famous biologist John Maynard Smith [40] who had a rather pragmatic view on the subject. He compares macroscopic biologists as pursuing a holistic strategy by means of a top-down approach to describe the phenomena observed in biology with the reductionists' program of molecular biologists who perform a bottom-up approach to interpret biological phenomena by the methods of chemistry and physics. He rejects holistic arguments boiling down to the claim that, because we do not understand some phenomena at present, there must be some special vital force, which is responsible for them. He says [40, p. vii]:

... As it happens, I do not understand how modern sewing-machines work, but this does not lead me to suppose that the laws of topology have been broken: Indeed, I feel confident I could find out if someone would let me take one into pieces....

Although the holistic view is preferable to John Maynard Smith, he makes a visionary statement about molecular biology [40, p. vii]:

... Holists are, I think, in a weaker position, if only because in recent years progress has been so much faster from the bottom up than from the top down. Yet I do share their conviction that there are laws that can only be discovered by research on whole organisms, and on populations of organisms. Almost all my own work has been done at those levels. What should be the attitude of a biologist working on whole organisms to molecular biology? It is, I think, foolish to argue that we are discovering things that disprove molecular biology. It would be more sensible to say to molecular biologists that there are phenomena that they will one day have to interpret in their terms. ....

The expectation of Maynard Smith has become almost true nowadays in systems biology. What is said here about chemistry and biology, I believe, is likewise true for the relation between neurobiology and psychology or population biology and sociology.

Recalling Ludwig Boltzmann's statements on evolution and biology [7, p. 29] we would assign him to the community of hierarchical reductionists. In other words he was convinced that one day the most complex biological phenomena would find their ultimate explanation in physics and chemistry of living matter. His high esteem of evolution makes clear his appreciation for phenomena that are unique in the realm of living beings, because self-organization and selection in the inanimate world were no theme in the nineteenth century. With our current knowledge the view is more subtle since we have plenty of examples for pattern formation, mode selection, and other spontaneous ordering processes in pure physics as well as fully developed theories to deal with them [45], [26], [27]. What distinguishes life sciences from the sciences

of inanimate matter is biological or genetic information and how it originates through evolution [19], [16], [20].

### 3 Molecular biology and evolution

The beginning of biochemistry and the start of the unification of chemistry of minerals and biology is commonly dated 1828 when Friedrich Wöhler succeeded to synthesize urea by heating the salt ammonium cyanate. For more than a century biochemists isolated, purified, and studied molecules obtained from living beings. The chemical compositions of biomolecules has been established. Biochemical reactions, in particular catalysis by means of enzymes, were investigated as rigorously as other chemical reactions and biochemical kinetics became an important field in its own right. A real breakthrough in understanding the molecules of life was the introduction of the concept of macromolecules by the German organic chemist Hermann Staudinger in the nineteen twenties. He was awarded the nobel prize in chemistry 1953. Staudinger characterized macromolecules as polymers consisting of a large number of small molecular units that are linked together by chemical bonds. He correctly recognized biological macromolecules, in particular proteins, nucleic acids and carbohydrates as heteropolymers built from several classes of monomeric units. The enormous variability of biopolymers is a result of combinatorics: A polymer of length  $n$  built from  $\kappa$  classes on monomers can exist in  $\kappa^n$  different sequences, each of which having the possibility to give rise to different molecular properties.

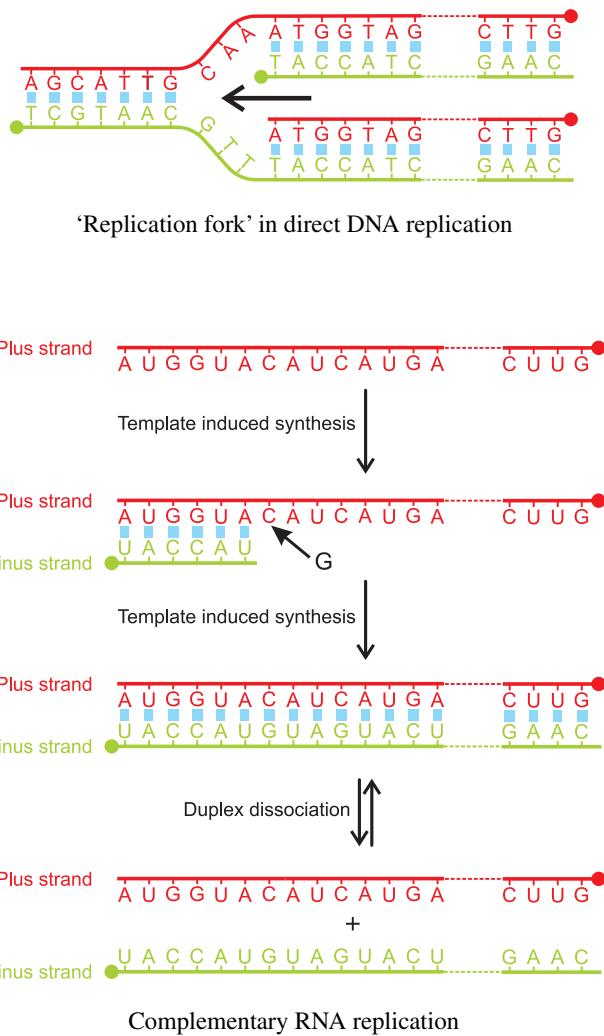
The second breakthrough in understanding the molecular mechanisms of life occurred after World War Two when the methods of structure determination through application of crystallography were extended to biomolecules. The two most important landmarks were: (i) The three-dimensional structural model for the DNA double helix by James Watson and Francis Crick and (ii) the determination of the spatial structures of the proteins myoglobin and hemoglobin at atomic resolution by John Kendrew and Max Perutz, respectively. All four researchers were awarded nobel prizes in 1962, Watson and Crick in medicine and Kendrew and Perutz in chemistry. A close look at the three-dimensional structures of biomolecules, in particular at the DNA double helix, gave immediate hints on their biological function. Watson and Crick state at the end of their seminal letter to Nature [69, see Figure 1]:

... It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material. ...

These structure determinations are seen as the beginning of molecular biology<sup>7</sup> and initiated the remarkable development of structural biology. Larger and larger structures were determined at atomic resolution and revealed Nature's tricks to perform the most sophisticated chemical reactions in highly specific and efficient ways. In very short time after the determination of DNA structure the whole genetic machinery including the

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<sup>7</sup>The fascinating story of the sequence of discoveries in molecular biology is told in Judson [30].



**Figure 1. Basic mechanisms of nucleic acid replication.** DNA replication (top) is a complex process involving a machinery of some twenty protein molecules. It is semi-conservative in the sense that every daughter molecule carries one strand of the parent DNA. RNA replication (bottom) commonly follows a complementary mechanism: A double-helical (plus-minus) duplex is synthesized from a (single) plus strand by making use of the complementarity of Watson-Crick base pairs. The critical step in replication is the separation of the duplex into two single strands because long double helical stretches are bound strongly. In RNA evolution experiments separation into single strand is performed by the replicase that prevents the formation of long double helical stretches through separating them into the two single strands that form their own structures.

genetic code relating DNA, RNA, and protein was discovered and in the early nineteen sixties molecular biology was fully established.

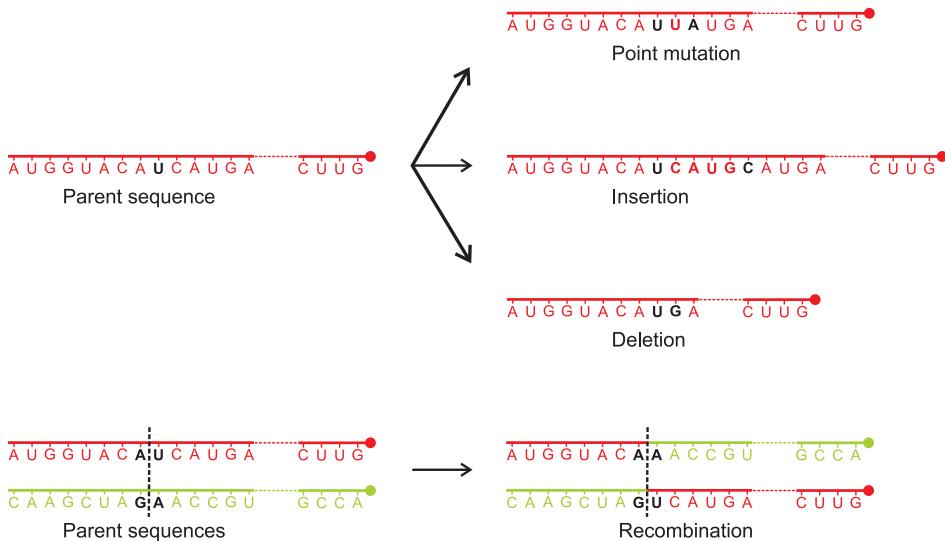
A third landmark in the development of molecular life sciences was the invention of new techniques for DNA sequencing by Walter Gilbert in USA and Frederick Sanger in England. Both received the nobel prize in chemistry 1980. Sequencing of whole genomes<sup>8</sup> of organisms became possible and molecular genetics got a new basis. The goal was now to investigate whole cells and whole multicellular organisms rather than individual biomolecules. Genomics, proteomics, metabolomics, and systems biology study all genes, all proteins, all metabolites, and all reactions of a cell or an organism together. The various *omics* aim at investigations of the chemistry of entire cells or organisms. The reductionistic bottom-up approach is currently reaching the situation John Maynard Smith was addressing in the quotation. Chemistry and physics have conquered biology but the physicists and chemists entering are becoming biologists, because they are now asking biological questions and they are analyzing the problems of biology with the new techniques they brought from their original disciplines. Notions and concepts genuine to biology find explanations in terms of chemistry and physics. Examples are Gregor Mendel's laws of inheritance and systematic deviations from the simple ratios, regulation of gene activities including pleiotropy and epistasis, epigenetic phenomena, and many others. Genetic information was found to be one of the most relevant properties distinguishing living and inorganic matter, others are homeostasis, resilience and many more.

The source of variation in populations has always been some kind of mystery. Charles Darwin, as we have said, believed in a kind of Lamarckian mechanism. Molecular genetics was able to explain all kinds of variations as types of chemical reactions giving rise to deviations from correct copying of DNA or RNA. In Figure 2 we summarize the most frequently occurring classes of mutations and recombination. Error prone replication and recombination are the sources of diversity in populations. When selected, mutations introduce genetic novelty in Nature.

Evolution in the Darwinian sense is based on multiplication, variation, and selection. All three prerequisites can be fulfilled by molecules outside a cellular environment. Therefore there is no reason why the observation of evolution should be restricted to organisms. Indeed, Sol Spiegelman was able to show already in the nineteen sixties that RNA molecules evolve in test-tubes provided an environment that supports replication is provided and consumed materials are replenished [43], [63]. He took a series of test-tubes filled with stock solution, which contains all substances that are required for Q $\beta$  viral RNA replication including an enzyme, Q $\beta$  replicase. A sample of viral RNA is injected into the first test-tube, replication starts, material is consumed, and after some while a small sample of this test-tube is transferred into test-tube no.2. The procedure is repeated over and over again and after a sufficiently large number of serial transfers an RNA molecule is isolated that replicates much faster than the original one. Selection for the fastest replicating molecule has taken place and, as sequence analysis shows, the faster replicating molecules are much smaller than the original viral RNA.

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<sup>8</sup>The genome or the genotype of an organism is the complete genetic information that is stored in its DNA.



**Figure 2. Basic mechanisms of sequence variation.** The upper part of the figure sketches three classes of mutations: (i) A point mutation where a single digit is changed and the sequence length remains constant, (ii) an insertion where part of the sequence is replicated twice, and (iii) a deletion where part of the sequence is not replicated. In the lower part we show a case of symmetric recombination between two sequences of equal lengths leading to two new sequences both with the same number of nucleotides – for the sake of simplicity recombination is shown here for two single stranded molecules; in case of two double stranded molecules the molecular mechanism is more complex. Asymmetric recombination (not shown) leads to sequences of different chain lengths. In recombination the genetic information of two parent strands is reassembled in the two daughter molecules.

The explanation is straightforward: The genes necessary for survival under natural conditions are not needed in the artificial laboratory environment and, therefore, they are eliminated through deletions yielding smaller and faster replicating molecules. Later on these experiments were repeated, carefully analyzed, and substantially extended [5], [6], [3], [4], [64], [47].

## 4 Modelling evolution of molecules

The success of evolutionary optimization is based on the dichotomy of genotype and phenotype. The genotype of an individual is its DNA or RNA sequence, the phenotype is the totality of its properties and consequently all variation, mutation or recombination, involves the genotype, whereas selection being based on fitness values or numbers of (fertile) offspring is a property of the phenotype. Commonly, the phenotype is a highly complex object but in case of serial transfer or flow reactor optimization of RNA, the

phenotype is the three-dimensional structure of the RNA molecules together with its properties in the laboratory experiments. In other words, variation operates on the genotype and selection weights fitness relative to mean fitness in the population. Here we review an attempt to see evolution with the glasses of a physicist [51], [22], [61].

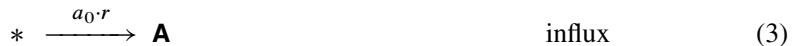
Definitions of genotype and phenotype spaces allow for a formalization of evolutionary processes. The genotype or sequence space  $\mathcal{Q}_n$  is a discrete space comprising all sequences of chain length  $n$  with the Hamming distance  $d_H(\mathbf{X}_i, \mathbf{X}_j)$  representing a metric.<sup>9</sup> The points in phenotype or shape space  $\mathcal{S}_n$  correspond to individual phenotypes and  $d_S(S_i, S_j)$  is some metric in phenotype space. Fitness values,  $f_k$ , are the result of two consecutive mappings from sequence space into shape space and from shape space into non-negative real numbers:

$$\begin{aligned} \psi: \{\mathcal{Q}_n; d_H(X_i, X_j)\} &\xrightarrow{\text{fold}} \{\mathcal{S}_n; d_S(S_i, S_j)\} \quad \text{or} \quad S_k = \psi(X_k), \\ \phi: \{\mathcal{S}_n; d_S(S_i, S_j)\} &\xrightarrow{\text{eval}} \mathbb{R}_+^1 \quad \text{or} \quad f_k = \phi(S_k). \end{aligned} \quad (2)$$

Evolution takes place in genotype *and* phenotype space: A population migrates in sequence space as a consequence of mutation and recombination, the population in genotype space is mapped by means of  $\psi$  into an ensemble of phenotypes, which in turn have their individual fitness values described by  $\phi$ . Based on this mapping  $\phi$  selection operating on the population through reducing the numbers of genotypes of less fit phenotypes and eventually eliminating them. Hence evolution can be understood as a process in two spaces where the dynamics is coupled through the two mappings  $\psi$  and  $\phi$ .

Studying evolution of molecules in the laboratory reduces the enormous complexity of *in vivo* conditions and allows for straightforward modelling by means of chemical kinetics. Mathematical analysis is possible for ODE based models. Stochasticity can be investigated by means of computer simulations. Here we shall sketch the theory of molecular evolution only briefly and supplement the rigorous results by computer simulations providing hints on statistics in evolution (Section 5).

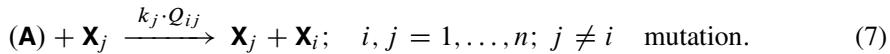
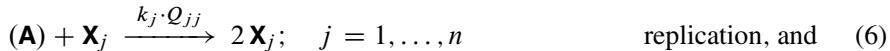
The currently simplest model systems for studying evolution *in vitro* are Spiegelman's experiment and various other selection assays [35]. For the mathematical model we choose a flow reactor (Figure 3) in which serial transfers are replaced by a continuous influx of stock solution containing  $\mathbf{A}$  at a concentration  $a_0$ . The influx is compensated in volume by an outflux of the reaction mixture:




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<sup>9</sup>The Hamming distance between two sequences,  $d_H(\mathbf{X}_i, \mathbf{X}_j)$  counts the number of the positions in which the two sequences  $\mathbf{X}_i$  and  $\mathbf{X}_j$  differ. Restriction of sequence spaces to constant chain length  $n$  has the consequence that only point mutations and symmetric recombinations are considered. Extensions to shape spaces with variable chain lengths are not simple but possible.

The symbol **A** stands for the material, which is consumed in the synthesis of the RNA molecules,  $\mathbf{X}_j$  ( $j = 1, \dots, n$ ). Dilution effects all molecular species in the same way. The parameter  $r$  represents the flow rate or, in other words,  $\tau = r^{-1}$  is the mean residence time of a volume element in the flow reactor. It is straightforward to show that complementary replication,  $\mathbf{A} + \mathbf{X}_+ \rightarrow \mathbf{X}_+ + \mathbf{X}_-$  and  $\mathbf{A} + \mathbf{X}_- \rightarrow \mathbf{X}_- + \mathbf{X}_+$  (Figure 1) is characterized by two phases: (i) an initial phase that leads to a stationary value of the relative amounts of both strands and (ii) a quasi-stationary phase, during which the two strands forming the plus-minus ensemble grow together with a rate parameter that is given by the geometric mean:  $k = k_{\pm} = \sqrt{k_+ \cdot k_-}$  [19], where  $k_+$  and  $k_-$  are the rate parameters for the individual strands. Replication and mutation are considered as parallel chemical reactions (Figure 4):



Although full reaction kinetics of RNA replication follows a complicated multistep mechanism [6], it is sufficient for our purposes to consider the overall processes (6) and (7). The material required for polymer synthesis is put in parentheses in order to indicate that commonly a mixture of compounds is needed and we dispense here from considering explicit stoichiometry. Then, the replication-mutation system is determined by a vector of replication rate parameters,  $\mathbf{k} = (k_1, k_2, \dots, k_n)$  and a matrix of mutation frequencies,

$$Q = \begin{pmatrix} Q_{11} & Q_{12} & \dots & Q_{1n} \\ Q_{21} & Q_{22} & \dots & Q_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ Q_{n1} & Q_{n2} & \dots & Q_{nn} \end{pmatrix}.$$

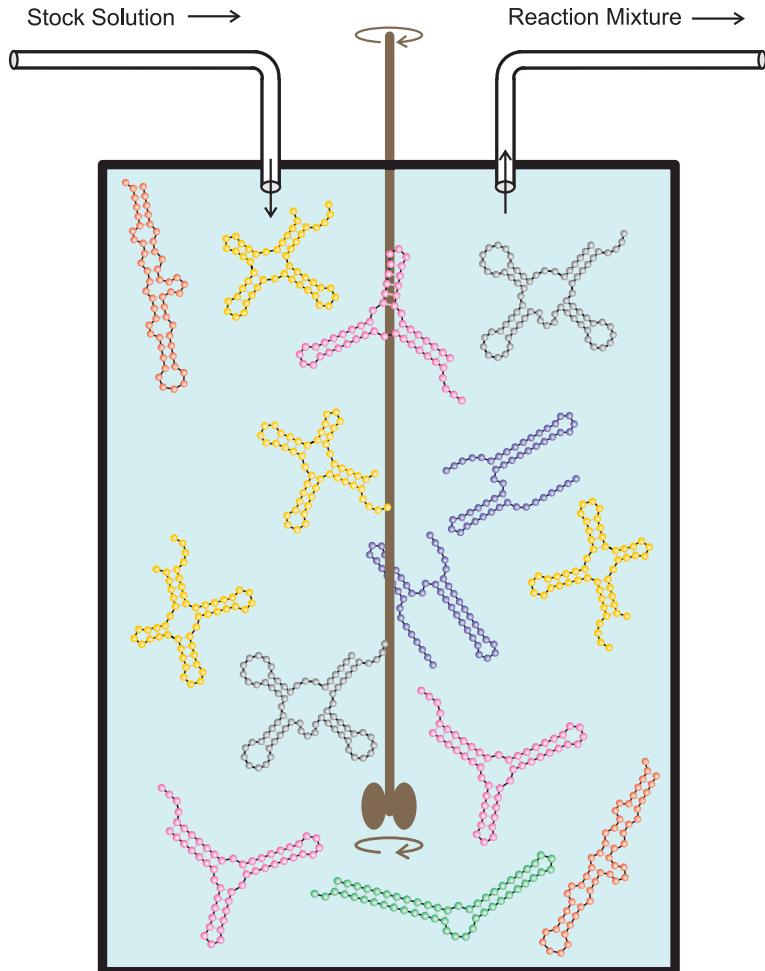
All components of  $\mathbf{k}$  and all entries of  $Q$  are real and nonnegative.<sup>10</sup> The matrix  $Q$  is a (column) stochastic matrix since every replication has to be either correct or not:  $\sum_{i=1}^n Q_{ij} = 1$ . A uniform error rate model is useful for studying replication-mutation systems in general or for cases where more detailed information is missing. Three assumptions are made: (i) Only point mutations are considered, (ii) the frequency of mutation does not depend on the particular kind of base exchange, and (iii) the frequency of mutation does not depend on the position of the mutated nucleotide in the sequence. Then, the mutation frequency from  $\mathbf{X}_j$  to  $\mathbf{X}_i$  can be computed from the chain length  $n$ , the single nucleotide error rate  $p$ , and the Hamming distance of  $\mathbf{X}_j$  and  $\mathbf{X}_i$ ,  $d_H(\mathbf{X}_i, \mathbf{X}_j)$ :

$$Q_{ij} = (1 - p)^{n - d_H(\mathbf{X}_i, \mathbf{X}_j)} p^{d_H(\mathbf{X}_i, \mathbf{X}_j)}. \quad (8)$$

Accordingly, the whole mutation matrix depends only on the relative position of the sequences in sequence space as expressed by the Hamming distance and on the single nucleotide error rate.

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<sup>10</sup>This is a consequence from chemical reaction kinetics where all rate parameters are real and nonnegative.



**Figure 3. The flow reactor as a device for studying *in vitro* evolution of molecules.** The reactor maintains off-equilibrium conditions by means of a influx of stock solution that supplies material (**A**) for replication. Molecules produced in excess are removes from the reaction mixture through an unspecific outflow. A population of  $N$  RNA molecules is subjected to replication and mutation. RNA structures are computed and evaluated by means of the function  $f_k = \phi(S_k)$  for all mutant sequences. The clover-leaf shaped yeast tRNA<sup>phe</sup> (grey shape in the reactor) was chosen as target structure. Inputs of an evolution experiment *in silico* are the parameters (i) population size  $N$ , (ii) chain length  $n$  of the RNA molecules, (iii) the mutation rate  $p$ , and (iv) the initial population.

The dependence of the rate of RNA synthesis on the concentration of the required material  $\mathbf{A}$ ,  $[\mathbf{A}] = a$ , is assumed to be some monotonically increasing function  $F(a)$ .<sup>11</sup> It is straightforward to write down the kinetic differential equation of replication and mutation for the mechanism of Figure 4 in the flow reactor shown in Figure 3 ( $[\mathbf{X}_j] = x_j$  with  $j = 1, \dots, n$ ):

$$\begin{aligned} \frac{da}{dt} &= -\sum_{j=1}^n k_j F(a) x_j + r (a_0 - a) \quad \text{and} \\ \frac{dx_j}{dt} &= \sum_{i=1}^n k_i Q_{ij} F(a) x_i + r x_j; \quad j = 1, \dots, n. \end{aligned} \quad (9)$$

The flow is adjustable and we can use programmed flow  $r(t)$  such that the concentration of  $\mathbf{A}$  becomes constant,  $a(t) \rightarrow \bar{a} = \text{const}$ . Straightforward computation yields

$$\begin{aligned} r(t) &= \frac{1}{\bar{c}} \sum_{i=1}^n f_i x_i(t) \quad \text{with } f_i = k_i F(\bar{a}) \text{ and } \bar{c} = a_0 - \bar{a} = \sum_{i=1}^n x_i, \\ \frac{dx_j}{dt} &= \sum_{i=1}^n f_i Q_{ij} x_i - x_j \bar{f}; \quad \bar{f} = \frac{\sum_{k=1}^n f_k x_k}{\bar{c}} \text{ and } j = 1, \dots, n. \end{aligned} \quad (10)$$

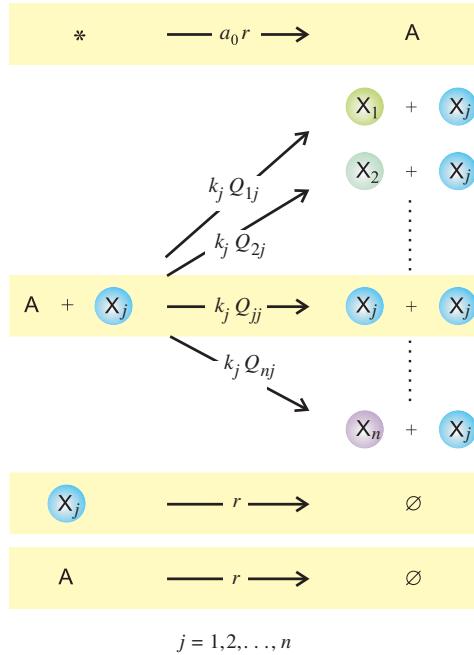
A transformation of the time axis with a strictly positive function does not change the outcome of the selection process [16], [58] and hence replication-mutation in the flow reactor and in the idealized system (10) lead to the same stationary distribution of RNA molecules.

Equation (10) has been studied in great detail as a model for selection based on replication and mutation [19], [16], [17], [18], [65], [59], [46], [15]. The cases with different behavior of the longtime solutions can be classified with respect to the properties of the value matrix  $W$ , which is derived from the vector  $\mathbf{f} = F(\bar{a}) \cdot \mathbf{k}$  and the mutation matrix  $Q$  according to equation (10):  $W \doteq \{f_i Q_{ij}; i, j = 1, \dots, n\}$ . We mention here the most important cases:

- (i) **Selection of single variant.** The vector  $\mathbf{f}$  has one single largest component ( $f_m > f_i; i = 1, \dots, n; m \neq i$ ),  $Q$  is diagonal and hence it is the unit matrix (all mutation rates are zero and we are dealing with replication alone).  $W$  is diagonal too and the variant  $\mathbf{X}_m$  with the largest fitness value,  $f_m = \max\{f_i; i = 1, \dots, n; m \neq i\}$ , called *master sequence*, is selected.
- (ii) **Selection of quasispecies.** The matrix  $W$  is primitive implying that Perron-Frobenius theorem holds [62, p. 3, p. 22],<sup>12</sup> and the error rate is below a threshold value  $p < p_{\max}$  (see iv). The population converges to a stationary state with a

<sup>11</sup>In case of simple stoichiometry  $F(a) = a$ .

<sup>12</sup>A nonnegative square matrix  $A = \{a_{ij}\}$  is said to be a *primitive* matrix if there exists  $k$  such that  $A^k \gg 0$ , i.e., if there exists  $k$  such that for all  $i, j$ , the  $(i, j)$  entry of  $A^k$  is positive. A sufficient condition for a matrix to be a primitive matrix is for the matrix to be an irreducible matrix with positive trace.



**Figure 4. Replication and mutation in the flow reactor.** Replication and mutation are considered as parallel chemical reactions. Stock solution containing  $\mathbf{A}$  at concentration  $a_0$  and all other material required for replication flows into the reactor with flow rate  $r$ . The volume compensating outflux reduces all concentrations with the same flow rate. The reaction rate parameter for a replication of template  $\mathbf{X}_j$  is denoted by  $k_j$ . The dimensionless factors  $Q_{ij}$  represent the probabilities for the synthesis of molecule  $\mathbf{X}_i$  as an error copy of template  $\mathbf{X}_j$ . Accordingly,  $Q_{jj}$  is the frequency of correct copying of  $\mathbf{X}_j$ . Since every copy has to be either correct or error prone, we have  $\sum_{i=1}^n Q_{ij} = 1$  and  $Q$  is a (column) stochastic matrix. The pure replication case is underlaid in yellow.

mutant distribution, which is determined by the largest eigenvector of matrix  $W$  corresponding to the largest eigenvalue  $\lambda_0$  with the following properties:

1.  $\lambda_0$  is real and strictly positive,
2.  $\lambda_0 > |\lambda_k|$  for all  $k \neq 0$ ,
3.  $\lambda_0$  is associated with strictly positive eigenvectors, and
4.  $\lambda_0$  is a simple root of the characteristic equation of  $W$ .

Hence, the unique stationary population consists of a master sequence and a distribution of mutants in which all variants are present.

- (iii) **Random drift through neutral evolution.** Drifting populations may be the result of neutrality in fitness values. Provided the degree of neutrality is sufficiently large the populations do not reach stationary distributions but drift randomly

through sequence space in the sense of neutral evolution [32], [29]. The process can be described successfully as diffusion of the population in sequence space.

- (iv) **Random drift through error accumulation.** No stationary population is approached if the error rate exceeds a threshold value,  $p > p_{\max} = 1 - \sigma_m^{-1/n}$ . Here  $\sigma_m$  denotes the superiority of the master sequence:

$$\sigma_m = f_m / \overline{f_{-m}} \quad \text{with} \quad \overline{f_{-m}} = \frac{\sum_{i=1, i \neq m} f_i x_i}{\sum_{i=1, i \neq m} x_i}.$$

If the critical value  $p_{\max}$  is exceeded maintenance of sequences in consecutive replications breaks down because of error accumulation.

Neutrality in the sense of (iii) has been postulated for the interpretation of mutation frequencies found in Nature [31], [33]. More than thirty years later discussions between so-called neutralists and selectionists claiming that the majority of non-deleterious mutations is selectively neutral or adaptive, respectively, have not yet come to an end in molecular evolution [39], [28], [48], [44]. Data on optimization of RNA based enzymes, so-called *ribozymes*, however, provide clear evidence for vast selective neutrality of RNA structures and properties [56] as it has been predicted earlier from large scale folding computations [57].

The random drift phenomenon described in (iv) is due to finite sizes of all real populations. The analysis of the stationary solution of the replication-mutation equation (10) in terms of the eigenvalues of the matrix  $W$  shows avoided crossing of two eigenvalues at the error threshold,  $p = p_{\max}$  [46]. At higher error rates ( $p > p_{\max}$ ) the largest eigenvector is very close to the uniform distribution,  $\bar{x}_1 = \bar{x}_2 = \dots = \bar{x}_m = \dots = \bar{x}_n$ . Maximum population sizes in evolution experiments with molecules are in the range of  $N = 10^{16}$  molecules, natural populations of viruses or bacteria are much smaller and hardly exceed  $N = 10^{10}$ . The numbers of possible sequences ( $n$ ), however, are much larger: For rather small chain length of one hundred,  $n = 4^{100} \approx 10^{60}$  different polynucleotide sequences are possible. Consequently,  $n \gg N$  and a uniform population can never exist. Instead, the population occupies only a tiny fraction of sequence space and mutation drives it to drift randomly.

The error threshold phenomenon (iv) turned out to be highly relevant for virology. In particular the maximum error rate sets a limit to the maximum length of sequences,  $n_{\max} \approx \ln \sigma_m / p$  which is reflected by an empirically found relation between replication accuracy and genome length in RNA viruses. Depending on the distribution of the fitness values  $f_k$  in sequence space the transition from the stationary quasispecies to the random drift regime may be sharp or smooth. The former case is fulfilled on sufficiently steep and rugged landscapes that give rise to a phase transition in sequence space. The latter case is found with smooth landscapes [71], [1].

The kinetic theory of molecular evolution in form of the quasispecies concept is based on two implicit assumptions: (i) infinite population size and (ii) sufficient time to reach the stationary distributions of variants. The first assumption is standard in chemical kinetics: Although we are never dealing with infinite populations fluctuations

become small for concentrations in molar range.<sup>13</sup> This is often not the case in biology where we have self-enhancing systems like replication, which amplify fluctuations. The second point is no problem in laboratory systems but may be important for coevolution in ecosystem, in particular in host-parasite systems.

## 5 Computer simulation of molecular evolution

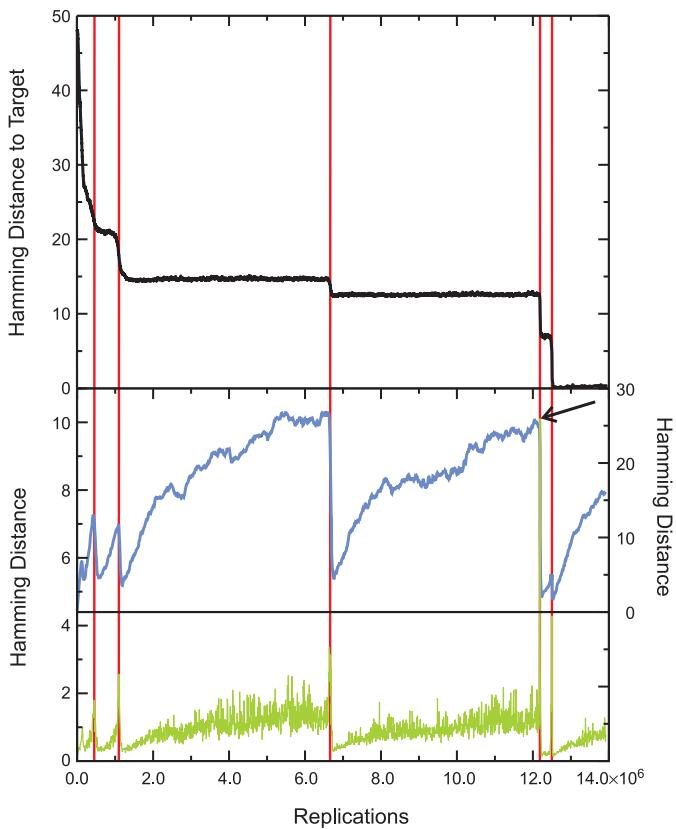
Computer simulations were performed in order to provide data for evolution on realistic biological fitness landscapes. Neither population genetics [28] nor the kinetic theory of evolution deal with intrinsic genotype-phenotype relations that allow for comprehensive analysis. For evolution of molecules such landscapes are provided by the mapping (2) for which suitable approximations exist [60]. The flow reactor (Figure 3) is used also for the computer simulations of RNA evolution [23]. Population sizes up to  $N = 100\,000$  can be handled. The algorithm applied [24], [25] computes individual trajectories, which simulate directly chemical reactions through encounters of molecules in homogeneous medium, gas phase or solution. Sampling of trajectories provides (statistical) approximations to the solutions of the corresponding Master equation. Accordingly, the time of computation is proportional to real time.

Basic results of the simulations are shown by means of a single trajectory showing the mean distance of the population from the target (Figure 5). Evolutionary optimization of RNA structure does not occur gradually but shows a stepwise or punctuated progress, which is the result of processes on two time scales. Fast adaptive phases during which the distance to target decreases are interrupted by long quasi-stationary epochs or plateaus with no progress in the approach to the target structure. Explanation of this finding is straightforward: The mapping of RNA sequences into structures is characterized by a high degree of neutrality and therefore the population spreads on a set of selectively neutral sequences within the time span of the horizontal plateaus. During this diffusion in sequence space many new genotypes are formed and the process continues until a mutant is found that allows for a continuation of the approach towards target. Adaptive phases are commonly initiated by a major rearrangement in structure that brings the population closer to the target structure. Examples of such major changes in structure are shown in Figure 6. It is worth mentioning that a similar stepwise optimization process has been observed with evolution of bacterial populations in serial transfer experiments under constant conditions [21], [50].

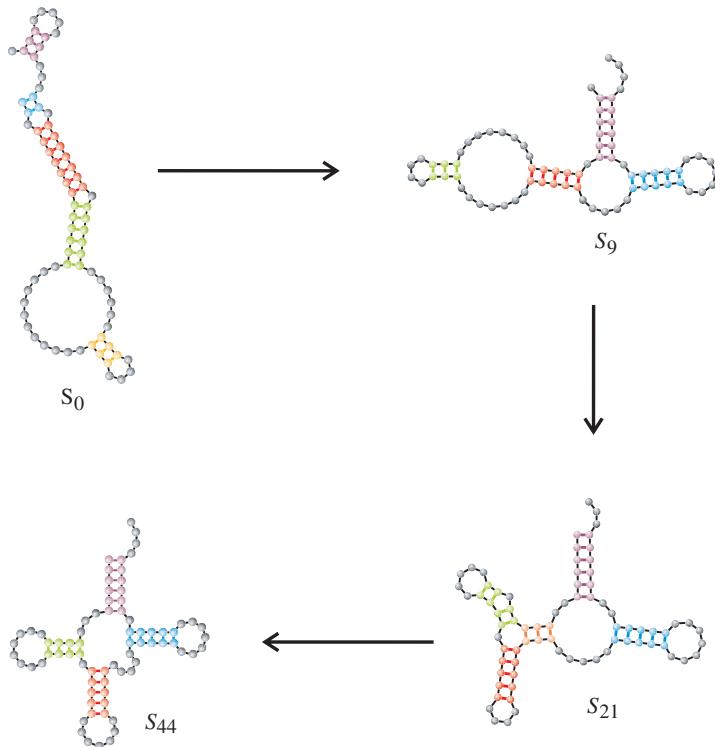
Sampling of trajectories and analysis revealed that (i) above a sharp threshold in population size around  $N = 16$  almost all trajectories reach the target structure, (ii) the particular sequence that forms the target structure  $S_T$  is almost always different in different simulations, and (iii) at population sizes above threshold the runtimes required to reach the target structure and the number of replications show vast scatter. Figure 7 presents mean values and error bars corresponding to  $\bar{t}_T \pm \sigma(t_T)$  where  $(t_T)_j$  is the

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<sup>13</sup>For all systems at equilibrium and for most chemical reactions the fluctuations are in the order of the square root of particle numbers:  $\bar{N} \pm \sigma(N) \pm \sqrt{\bar{N}}$ . For one mole particles  $\bar{N} \approx 6 \times 10^{23}$  and  $\sigma(N) \approx 8 \times 10^{11}$ , which is too small to detect.



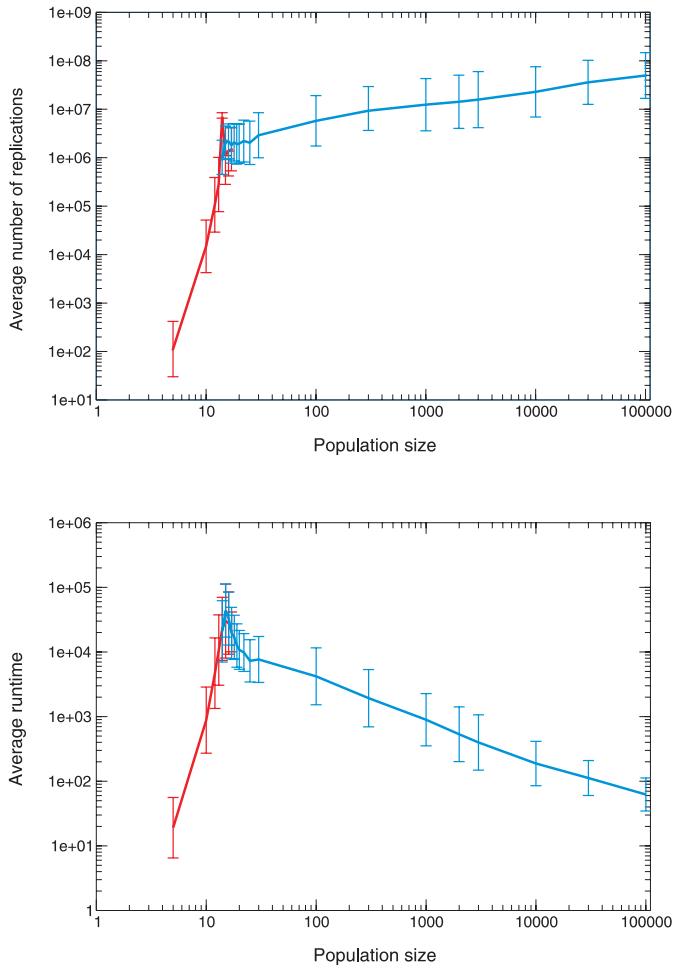
**Figure 5. Evolutionary optimization of RNA structure.** Shown is a single trajectory of a simulation of RNA optimization towards a tRNA<sup>phe</sup> target with population size  $n = 3000$  and mutation rate  $p = 0.001$  per site and replication. The figure shows as functions of time: (i) the distance to target averaged over the whole population,  $\overline{d}_S(S_i, S_T)(t)$  (black), (ii) the mean Hamming distance within the population,  $\overline{d}_P(t)$  (blue, right ordinate), and (iii) the mean Hamming distance between the populations at time  $t$  and  $t + \Delta t$ ,  $\overline{d}_C(t, \Delta t)$  (green) with a time increment of  $\Delta t = 8\,000$ . The end of plateaus (vertical red lines) are characterized by a collapse in the width of the population and a peak in the migration velocity corresponding to a jump in sequence space. The arrow indicates a remarkably sharp peak of  $d_C(t, 8\,000)$  around Hamming distance 10 at the end of the second long plateau ( $t \approx 12.2 \times 10^6$  replications). In other words, every adaptive phase is accompanied by a drastic reduction in genetic diversity,  $d_P(t)$ . The diversity increases during quasi-stationary epochs. On the plateaus the center of the cloud migrates only at a speed of Hamming distance 0.125 per 1 000 replications.



**Figure 6. Intermediate structures of structure optimization in the flow reactor.** We show the initial structure  $S_0$ , structure  $S_9$ , which is characterized by a particularly long plateau in the trajectory, structure  $S_{21}$  that is one step before the formation of the cloverleaf, and the target structure  $S_{44}$ .

time at which trajectory ‘ $j$ ’ reaches the target and ‘ $\sigma^2(t_T)$ ’ represents the variance or the square of the standard deviation of the first passage times to target. In contrast to the common  $\sqrt{N}$  law for standard deviations, here the scatter remains large with increasing population size. The mean number of replications increases slightly with population size whereas we observe a pronounced decrease in the time to reach target when the population becomes larger. The take-home lesson for carrying out evolution in the test-tube is therefore: Large population sizes should be applied if time is the limiting factor but population sizes as small as possible are recommended when the limitation lies in the material resources.

A recent computer simulation [36] using the flow reactor, trajectory sampling and a similar RNA target as in [23] proved the existence of the error threshold predicted by the kinetic theory of molecular evolution.



**Figure 7. Scatter in length of trajectories in evolutionary optimization.** The stochastic process underlying the simulation has only two absorbing states: (i) extinction,  $\Upsilon_0$ :  $\{X_i = 0 \text{ for all } i = 1, 2, \dots, n\}$ , and (ii) successful approach to target,  $\Upsilon_1$ :  $\{\text{there exists } \mathbf{X}_k \text{ such that } \psi(\mathbf{X}_k) = S_T \text{ and } X_k \neq 0\}$ . Hence, trajectories end either in  $\Upsilon_0$  or in  $\Upsilon_1$ . The two plots show the average number of replications (top) or the average runtime (bottom) to reach either  $\Upsilon_0$  (red) or  $\Upsilon_1$  (blue). The transition from almost all trajectories going to  $\Upsilon_0$  to almost all trajectories going to  $\Upsilon_1$  is sharp and lies in the range between  $N = 13$  and  $N = 19$ . The error bars refer to  $\pm\sigma$  with  $\sigma$  being the standard deviations in log-normal distributions.

## 6 Concluding remarks

The great success of Ludwig Boltzmann was to introduce proper statistics that starts out from random molecular encounters and leads to the deterministic quantities of thermodynamics. As expressed by the  $\sqrt{N}$ -law, fluctuations that are highly important at low particle numbers become negligibly small at molar concentrations. Self-enhancement, in particular when it is caused by reproduction, gives rise to different laws for fluctuations and introduces indeterminism on macroscopic scales. A prominent example is the hypothetical approach to the uniform distribution where the number of possible molecular species exceeds the accessible population sizes by many orders of magnitude (Section 4). The problems that were encountered in attempts to do proper statistics in evolution provide, at the same time, the basis for the enormous diversity and beauty of Nature. Biological information space built upon sequence diversity is inexhaustible.

Since its spectacular beginnings in 1953 molecular biology revealed piece after piece the magnificent chemistry and physics of life. Determinations of three-dimensional molecular architectures progressed to larger and larger units and provided deep insights into the mysteriously successful chemistry performed by cells and organisms in the sense of Ludwig Boltzmann's statement cited in the beginning of this chapter [7, p. 41]. The new developments initiated in the nineteen eighties pushed molecular biology and molecular genetics up to the level of entire cells or organisms: Genomics, proteomics, metabolomics, and systems biology are aiming at determining and analyzing all genes, all proteins and their interactions, all metabolic reactions and eventually the dynamics of complete regulatory and synthesizing networks.

In a way John Maynard Smith's vision [40, p. vii] has become reality. The reductionists' programm has reached a state where cellular and organismic problems can be handled on the molecular level. The new discipline systems biology [34], [49] aims at modelling complete genetic regulatory and metabolic networks of whole cells. Holistic questions like homeostasis, autopoiesis, cell cycle regulation, circadian rhythms and many others can now be addressed by the molecular approach. Explanations can be given by means of known processes at the lower hierarchical level that is biochemistry and chemical kinetics. The physicists and the chemists who have entered biology became biologists while studying biological problems with the techniques they brought with them from their original fields of research.

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Duino Rilke Walk 2006  
(Courtesy of Wolfgang L. Reiter)

# Ludwig Boltzmann – the restless prophet

Wolfgang L. Reiter

Ludwig Boltzmann (1844–1906) died just over a century ago. He belongs to a select group of great scientists whose concepts and work remain at the center of significant work in theoretical physics today. This is particularly remarkable, because the most fertile period of Boltzmann’s work was during the last quarter of the 19th century.

As a member of the Commission for the Investigation of Radioactive Substances of the Vienna Academy of Sciences<sup>1</sup> Boltzmann must have felt deep satisfaction that the atomic picture of matter he championed slowly gained first experimental support through the discoveries of *X*-rays, radioactivity, and the electron at the end of the 19th century. Further, Albert Einstein (1879–1955) stood on Boltzmann’s shoulders in 1905 when he proposed his revolutionary light-quanta hypothesis, his method for determining the dimensions of molecules, and his theory of Brownian motion.<sup>2</sup> Boltzmann thus lived on the watershed between 19th and 20th-century physics.<sup>3</sup> Rooted in the Newtonian tradition with its mechanical models, he stands between James Clerk Maxwell (1831–1879), whom he admired enormously, and the young Einstein, whom he would have embraced as his true heir had he been aware of Einstein’s groundbreaking achievements of 1905.

Boltzmann’s firm belief in the existence of atoms was deeply rooted in his confidence in the Newtonian mechanical worldview. To understand the macroscopic properties of matter, in particular those of gases, Boltzmann took a decisive step of great simplicity, applying statistical arguments to determine the properties of states in thermal equilibrium and their dynamical evolution. The Boltzmann equation and its rich mathematical structure are still hot topics today in statistical physics, and the origin of its asymmetry

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<sup>1</sup>This Commission (*Komission für die Untersuchung radioaktiver Substanzen*), chaired by Franz S. Exner (1849–1926), was founded in 1901 to foster research of the newly discovered phenomenon of radioactivity as well as international co-operation in this field. The Commission ordered the production of 4 grams of radium chloride by the Auer von Welsbach plant in Atzgersdorf near Vienna between 1904 and 1907, using pitchblende residues from the uranium mines in St. Joachimsthal. This huge amount of radium provided the basis for Vienna in becoming one of the centers of early radioactivity research, together with Marie and Pierre Curie in Paris, Ernest Rutherford in Manchester and later Cambridge, and Lise Meitner and Otto Hahn in Berlin. The Vienna Radium Institute, the first institute world wide exclusively dedicated to radioactivity research, opened doors in 1910 under the executive directorship of Stefan Meyer. On Meyer see Wolfgang L. Reiter, *Stefan Meyer und die Radioaktivitätsforschung in Österreich*. Österreichische Akademie der Wissenschaften, Anzeiger der phil.-hist. Kl., 135. Jg., 2000, 105–143.

<sup>2</sup>For a recent discussion of Einstein’s 1905 papers, see John S. Rigden, *Einstein 1905: The Standard of Greatness* (Cambridge, Mass. and London: Harvard University Press, 2005). New translations of Einstein’s five major papers of 1905 into modern English had recently been published in *Einstein’s Miraculous Year. Five Papers That Changed the Face of Physics*. Edited and introduced by John Stachel. (Princeton: Princeton University Press, 1998).

<sup>3</sup>David Lindley, *Boltzmann’s Atom: The Great Debate That Launched a Revolution in Physics* (New York: Free Press, 2001).

in time can only be understood properly when its initial conditions are viewed on a cosmological time scale.<sup>4</sup>

## Early life and education, 1844–1869

Ludwig Boltzmann was born just outside the city walls of Vienna at what was then Landstrasse 286 on February 20, 1844 – that very night marking the passage from Shrove Tuesday to Ash Wednesday. Ever the wry rationalist, he later commented that he was “born between happiness and depression”. His life was indeed marked by alternating periods of euphoria and depression, and embraced a love of music and an interest in public affairs. He was born at a cultural and political watershed in Austria: Johann Strauss the younger (1825–1899) gave his first public performance at the Café Dommayer near the Schönbrunn palace in Vienna in 1844, and the failed revolution of 1848 in Austria (and in other European countries) ushered in a period of Habsburg absolutism after Emperor Ferdinand I (1793–1875) was succeeded by Emperor Franz Joseph I (1830–1916).

Boltzmann was educated mainly by monks at the Akademisches Gymnasium in Linz, a provincial city in Upper Austria where his father Ludwig was a civil servant in the state financial administration. Here his son took piano lessons from Anton Bruckner (1824–1896) and developed his lifelong interest in music. His father’s premature death in 1859 must have deeply wounded his youthful psyche. Nonetheless, he passed his final Gymnasium examinations, the Matura, with distinction in 1863 and then matriculated at the University of Vienna to study mathematics and physics. Its Institute of Physics was located in the III District of Vienna and even in the same quarter, at Landstrasse 104 (now Erdbergstrasse 15), where he had been born.

Boltzmann received his Ph.D. degree three years later, in December 1866, which at that time did not require a written doctoral dissertation. Already that October he had become assistant to his teacher Josef Stefan (1835–1893), who decisively shaped his student’s scientific outlook and introduced him to his own field of research, gas theory.<sup>5</sup> Together with Hermann von Helmholtz (1821–1894), Stefan was the second early supporter of Maxwell’s theory of electromagnetism on the continent. No wonder that Boltzmann’s first publication of 1865 dealt with an application of Maxwell’s theory.<sup>6</sup> His second publication one year later was on the relationship of the second law of thermodynamics to the principles of mechanics and set the tone for his lifelong work in kinetic theory and statistical mechanics.<sup>7</sup> At Stefan’s institute he met Josef

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<sup>4</sup>Roger Penrose, *The Emperor’s New Mind: Concerning Computers, Minds, and the Laws of Physics* (New York and Oxford: Oxford University Press, 1989), Chapter 7.

<sup>5</sup>John Crepeau, “Josef Stefan: His life and legacy in the thermal sciences”, *Experimental Thermal and Fluid Science* **31**, Issue 7 (2007), pp. 795–803.

<sup>6</sup>Ludwig Boltzmann, “Über die Bewegung der Elektrizität in krummen Flächen”, *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften. Mathematisch-naturwissenschaftliche Classe. II. Abteilung* **52** (1865), 214–221; reprinted in *Wissenschaftliche Abhandlungen*, Band I, 1865–1874, ed. Fritz Hasenöhrl (Leipzig: J. A. Barth, 1909; reprinted New York: Chelsea, 1968), pp. 1–8.

<sup>7</sup>Idem, “Über die mechanische Bedeutung des zweiten Hauptsatzes der Wärmetheorie”, *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **53** (1866), 195–220; reprinted in *Wissenschaftliche Abhandlungen*,

Loschmidt (1821–1895), since 1868 Professor extraordinary (*ausserordentlicher Professor*) and four years later full (*ordentlicher*) Professor of Physics and a dedicated atomist.<sup>8</sup> Loschmidt, a generation older than Boltzmann, became his fatherly friend and exerted a lasting influence on him.<sup>9</sup>

In 1868, at the age of twenty-four, Boltzmann took the next step in his academic career, becoming Lecturer (*Privatdozent*) of Mathematical Physics at the University of Vienna. Much later he recalled this period in his life with great nostalgia.

*[The Institute of Physics at] Erdberg has remained for all my life a symbol of honest and inspired experimental work. When I [later] succeeded in injecting a bit of life into the Institute of [Physics at] Graz I used to call it, jokingly, Little Erdberg. By this I did not mean that the available space was scarce, because it was quite ample, probably twice as much as in Stefan's Institute [of Physics]; but I had not succeeded in equalling the spirit of Erdberg as yet. Even in Munich, when young PhDs came to tell me that they did not know what to work on, I used to think: How different we were in Erdberg! Today there is beautiful experimental apparatus and people are looking for ideas on how to use it. We always had plenty of ideas and were only preoccupied with the lack of equipment.<sup>10</sup>*

In one of his – as usual – rather lengthy papers that he published in 1868 (this one is 44 pages long)<sup>11</sup>, Boltzmann worked out a generalization of Maxwell's velocity-distribution law under the assumption that external forces (for example, gravity) were present and arrived at an expression that is now called the Boltzmann factor  $e^{-E/kT}$ , where  $E$  is the total energy,  $T$  is the absolute temperature, and  $k$  is the Boltzmann constant – an expression that is ubiquitous today in science and technology.

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Band I (ref. 6), pp. 9–33.

<sup>8</sup>For discussions of Loschmidt's life and work, including a bibliography of his publications, see W. Fleischhacker and T. Schönfeld, ed., *Pioneering Ideas for the Physical and Chemical Sciences: Josef Loschmidt's Contributions and Modern Developments in Structural Organic Chemistry, Atomistics, and Statistical Mechanics. Proceedings of the Josef Loschmidt Symposium, held June 25–27, 1995, in Vienna, Austria* (New York and London: Plenum Press, 1997).

<sup>9</sup>While the number of molecules per unit volume of a gas at standard temperature and pressure is generally known as Avogadro's number, Boltzmann, on the occasion of the unveiling of Loschmidt's bust at the University of Vienna in 1899, proposed that this number be called Loschmidt's number, a term that is sometimes still used in German-speaking countries.

<sup>10</sup>Ludwig Boltzmann, "Josef Stefan", in *Populäre Schriften* (Leipzig: Verlag J. A. Barth, 1905), pp. 92–103; on pp. 100–101. Quoted in Carlo Cercignani, *Ludwig Boltzmann: The Man Who Trusted Atoms* (Oxford and New York: Oxford University Press, 1998), p. 6.

<sup>11</sup>Ludwig Boltzmann, "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten", *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **58** (1868), 517–560; reprinted in *Wissenschaftliche Abhandlungen*, Band I (ref. 6), pp. 49–96. For the velocity-distribution law, see J. Clerk Maxwell, "On the Dynamical Theory of Gases", *Philosophical Transactions of the Royal Society of London* **157** (1867), 49–88; reprinted in *The Scientific Papers of James Clerk Maxwell*, W. D. Niven, ed., Vol. 2 (Cambridge: Cambridge University Press, 1909; reprinted New York: Dover, 1965), pp. 26–78.

## At the zenith: Professor in Graz, Vienna, Graz, 1869–1890

In 1869 the twenty-five-year-old Boltzmann was appointed Professor of Mathematical Physics at the University of Graz, a position he held for four years, until 1873. This was Boltzmann's first period in Graz and was marked by two fundamental scientific breakthroughs that he published in 1872 in his paper, "Further Studies on the Thermal Equilibrium of Gas Molecules",<sup>12</sup> namely, his *H*-theorem (*H* being the negative of the thermodynamic entropy *S*) and his eponymous transport equation. Boltzmann took his *H*-theorem to prove that the entropy *S* of the universe always increases; it was greeted by fierce objections, first in 1876 by his teacher and friend Loschmidt, who pointed out that it embodied a "reversibility paradox",<sup>13</sup> and two decades later, in 1896, by the German mathematician Ernst Zermelo (1871–1953), who called attention to the so-called "recurrence paradox".<sup>14</sup> Both objections forced Boltzmann to reexamine and elaborate his basic assumptions;<sup>15</sup> the first objection soon led him to his pioneering statistical interpretation of the second law of thermodynamics.

Boltzmann was one of the new breed of theoretical physicists, although no clear-cut division existed at the time between theoretical and experimental physicists. In fact, while Boltzmann's theoretical work is universally known, his small but nevertheless fruitful experimental work is not.<sup>16</sup> Despite his poor eyesight, Boltzmann was a talented experimentalist and enjoyed showing sophisticated mechanical experiments of his own design in his lectures.<sup>17</sup> Further, his early and strong interest in Maxwell's electrodynamics led him to investigate the dielectric constants of solids and gases and to experimentally confirm Maxwell's relation,  $n^2 = \epsilon\mu$  (where *n* is the index of refraction,  $\epsilon$  the dielectric constant, and  $\mu$  the permeability) in 1873–1874, while working in Helmholtz's laboratory in Berlin and in his own laboratories in Graz and Vienna.<sup>18</sup>

<sup>12</sup>Idem, "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen", *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **66** (1872), 275–370; reprinted in *Wissenschaftliche Abhandlungen*, Band I (ref. 6.), pp. 316–402.

<sup>13</sup>J. Loschmidt, "Über den Zustand des Wärmegleichgewichtes eines Systems von Körpern mit Rücksicht auf die Schwerkraft. I", *Sitzungsber. d. k. Akad. Wissen. Math.-naturw. Cl. II. Abt.* **73** (1876), 128–139; idem, "II", *ibid.*, 366–372; *idem*, "III", *ibid.* **75** (1877) 287–298; *idem*, "IV", *ibid.* **76** (1877), 209–225; Herbert Spohn, "Loschmidt's Reversibility Argument and the H-Theorem", in Fleischhacker and Schönfeld, *Pioneering Ideas* (ref. 8), pp. 153–157.

<sup>14</sup>Heinz-Dieter Ebbinghaus, *Ernst Zermelo: An Approach to his Life and Work*. (Berlin–Heidelberg–New York: Springer-Verlag 2007). For a discussion and excerpts of the original papers by Henri Poincaré, Ernest Zermelo, and Ludwig Boltzmann, see Stephen G. Brush, *Kinetic Theory. Vol. 2. Irreversible Processes* (Oxford: Pergamon Press, 1966), pp. 194–228.

<sup>15</sup>For a discussion of the reversibility and recurrence paradoxes within the context of Boltzmann's work, see Stephen G. Brush, "Ludwig Boltzmann and the Foundations of Natural Science", in Ilse M. Fasol-Boltzmann, ed., *Ludwig Boltzmann. Prinzipien der Naturphilosophie. Lectures on Natural Philosophy 1903–1906* (Berlin and Heidelberg: Springer-Verlag 1990), pp. 43–61, esp. pp. 48–50.

<sup>16</sup>Boltzmann's scientific oeuvre comprises 192 titles out of which 10 are on experimental topics; 23 publications can be categorized as popular writings. Besides that he published six monographs and edited J. C. Maxwell's *Über physikalische Kraftlinien*.

<sup>17</sup>Klemens Rumpf and Petra Granitzer, "Ludwig Boltzmann als Experimentalphysiker", *Physik in unserer Zeit* **5** (2006), 228–234.

<sup>18</sup>Ludwig Boltzmann, "Experimentelle Bestimmung der Dielektrizitätskonstante von Isolatoren", *Sitzungsber. d. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **67** (1873), 17–80; *idem*, "Experimentelle Bestim-

He thus provided the first experimental evidence for the validity of Maxwell's theory of light much earlier than Heinrich Hertz (1857–1894) did in his classic experiments in 1887–1888.

In 1873 Boltzmann met Henriette von Aigentler (1854–1938), the first female student at the University of Graz, and soon became engaged to her. That same year he accepted the position of Professor of Mathematics at the University of Vienna, which was a major step upward in his career within the Austro-Hungarian academic hierarchy. (The letters that he and his fiancé exchanged between Vienna and Graz have been published by Boltzmann's grandson, Dieter Flamm.<sup>19</sup>) Three years later, in 1876, Boltzmann returned to the University of Graz as Professor of Physics, married Henriette, and bought and refurbished an old farmhouse in Oberkroisbach on the outskirts of Graz, where he kept a cow to provide fresh milk for their children.

Boltzmann's second period in Graz, which lasted from 1876 until 1890, was marked by further groundbreaking scientific contributions. In 1877, at the age of thirty-three years, Boltzmann published his statistical interpretation of the second law of thermodynamics, which Einstein termed the Boltzmann principle: The entropy  $S$  of a macrostate (as determined by its pressure, temperature, and other variables) is proportional to the logarithm of the number  $W$  of microstates (as determined by the positions and velocities of all of the atoms), that is,  $S = k \log W$ .<sup>20</sup> The constant of proportionality  $k$ , known universally as the Boltzmann constant, was first evaluated by Max Planck (1858–1947) in 1900.<sup>21</sup> The formula  $S = k \log W$  is engraved on Boltzmann's tombstone in the Central Cemetery (*Zentralfriedhof*) in Vienna.<sup>22</sup>

In 1884 Boltzmann proved a conjecture of Stefan's, that the total energy emitted by a black body is proportional to the fourth power of its absolute temperature, which provided further support for Maxwell's electromagnetic theory. Stefan had recognized the importance of Maxwell's theory and had introduced his first and most gifted student

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mung der Dielektrizitätskonstante einiger Gase”, *ibid.* **69** (1874), 795–813; *idem*, “Über einige an meinen Versuchen über die elektrostatische Fernwirkung dielektrischer Körper anzubringende Korrekctionen”, *ibid.* **70** (1874), 307–341; reprinted in *Wissenschaftliche Abhandlungen*. Band I (ref. 6.), pp. 411–471, 537–555, 556–586.

<sup>19</sup> Dieter Flamm, ed., *Hochgeehrter Herr Professor! Innig geliebter Louis! Ludwig Boltzmann, Henriette von Aigentler, Briefwechsel* (Wien, Köln, Weimar: Böhlau, 1995).

<sup>20</sup> Ludwig Boltzmann, “Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung, respective den Sätzen über das Wärmegleichgewicht”, *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **76** (1877), 373–435; reprinted in *Wissenschaftliche Abhandlungen*, Band II, 1875–1881, ed. Fritz Hasenöhrl (Leipzig: J. A. Barth, 1909; reprinted New York: Chelsea, 1968), pp. 164–223; Albert Einstein, “Über einen die Erzeugung und Verwandlung des Lichts betreffenden heuristischen Gesichtspunkt”, *Annalen der Physik* **17** (1905), 132–148, on 140; reprinted in John Stachel, ed. *The Collected Papers of Albert Einstein*, Vol. 2, *The Swiss Years: Writings, 1900–1909* (Princeton: Princeton University Press, 1989), pp. 150–166, on p. 158. For a discussion, see Martin J. Klein, “The Development of Boltzmann's Statistical Ideas”, in E. G. D. Cohen and W. Thirring, ed., *The Boltzmann Equation: Theory and Applications* (Wien and New York: Springer-Verlag, 1973) [*Acta Physica Austriaca, Supplementum X* (1973)], pp. 53–106.

<sup>21</sup> Martin J. Klein, “Max Planck and the Beginnings of the Quantum Theory”, *Archive for History of Exact Sciences* **1** (1962), 459–479, esp. 471.

<sup>22</sup> For this and other scientific sites of Vienna, see Wolfgang L. Reiter, “Vienna: A Random Walk in Science”, *Physics in Perspective* **3** (2001), 462–489.

to it. As Carlo Cercignani has noted, that same year Boltzmann

*also wrote a fundamental paper, [<sup>23</sup>] generally unknown to the majority of physicists, who by reading only second-hand reports are led to the erroneous belief that Boltzmann dealt only with ideal gases; this paper clearly indicates that he considered mutually interacting molecules as well, with non-negligible potential energy, and thus ... it is he and not Josiah Willard Gibbs (1839–1903) who should be considered as the founder of equilibrium statistical mechanics and of the method of ensembles.*<sup>24</sup>

Three years later, in 1887, Boltzmann built upon an earlier work of 1884 and formulated the ergodic hypothesis.<sup>25</sup> He was then at the mature age of a forty-three years old professor and father of a happy family of four children.<sup>26</sup>

By this time Boltzmann was a scientific celebrity who attracted foreign students to Graz, such as the future Nobel Laureates Svante Arrhenius (1859–1927) and Walther Nernst (1864–1941), to study with the acknowledged European master of thermodynamics, statistical mechanics, and kinetic theory. Here, then, was a man flushed with professional success, enjoying a happy family life with his wife, his children, and a dog at his farmhouse in Oberkroisbach. Yet, dark clouds began to gather over this rosy Graz idyll. Several events conspired to undermine Boltzmann's mental stability and precipitate his long slide into depression. His beloved mother died in 1885. Three years later, he was elected Rector of the University of Graz and soon thereafter was confronted by a month of aggressive protests by German nationalist students. Next, without informing the Austrian authorities officially, Boltzmann accepted the prestigious Berlin chair of theoretical physics that had been vacated by the death of Gustav Kirchhoff (1824–1887), but he subsequently reneged, offering somewhat unconvincing reasons – his myopia, the lack of a comprehensive written plan for a lecture course he was to give in theoretical physics, and the absence of a significant group of mathematical physicists in Berlin. Probably the most damaging blow to him, however, was the death of his eleven-year-old son Ludwig from misdiagnosed appendicitis in 1889.

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<sup>23</sup>Ludwig Boltzmann, “Über die Eigenschaften monozyklischer und anderer damit verwandter Systeme”, *Journal für reine und angewandte Mathematik (Crelles Journal)* **98** (1884), 68–94; also in *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **90** (1884), 231. In this paper he introduced the term “Monode” for what today is called a stationary statistical ensemble. Cercignani is referring to the following but wrong article *idem*, “Über die Möglichkeit der Begründung einer kinetischen Gastheorie auf anziehende Kräfte allein”, *Sitzungsber. d. k. Akad. d. Wissen. Math.-naturw. Cl. II. Abt.* **89** (1884), 714–722; reprinted in *Wissenschaftliche Abhandlungen*, Band III, 1882–1905, ed. Fritz Hasenöhrl (Leipzig: J. A. Barth, 1909; reprinted New York: Chelsea, 1968), pp. 101–109. A critical examination of the 1884 paper by Boltzmann together with a highly informative discussion of the etymology of the word “ergodic” and its implications is given in Giovanni Gallavotti, “Ergodicity, ensembles, irreversibility in Boltzmann and beyond”, *Journal of Statistical Physics* **78** (1995), 1571–1589.

<sup>24</sup>Cercignani, *Ludwig Boltzmann* (ref. 10), p. 18 and Chapter 7.

<sup>25</sup>For a discussion of Boltzmann's and Maxwell's introduction of the ergodic hypothesis, with references to the original literature, see Stephen G. Brush, “Foundations of Statistical Mechanics 1845–1915”, *Arch. Hist. Ex. Sci.* **4** (1967), 145–183, esp. 168–177; reprinted in Stephen G. Brush, *The Kind of Motion We Call Heat*. Book 2. Statistical Physics and Irreversible Processes (Amsterdam, New York, Oxford: North-Holland, 1976), pp. 335–385, esp. pp. 363–377.

<sup>26</sup>Ludwig Hugo (1878–1889), Henriette (1880–1945), Arthur Ludwig (1881–1952), Ida Katharina (1884–1910); a fifth child, Elsa (1891–1966), was born while the Boltzmann's stayed in Munich.

## The restless Professor: Munich, Vienna, Leipzig, Vienna, 1890–1902

Boltzmann's neurasthenia (as it was then called) could no longer be ignored.<sup>27</sup> His decisions were progressively marked by restlessness and a sort of escapism probably triggered by his feeling of increasing isolation in Graz. He revived his interest in moving to Berlin and announced his desire to leave Graz, hoping that such a change in his life would calm his mental instability and insecurity. Then, again abandoning his idea of moving to Berlin, he accepted the chair of theoretical physics at the University of Munich in 1890, after spending eighteen years in Graz. His restlessness subsided in Munich, but he was haunted by homesickness for his native Austria. Three years later, Stefan died and the Viennese physicists immediately agreed to try to persuade Boltzmann to return to his *alma mater* as Stefan's successor. Boltzmann hesitated for two long years, but finally accepted the chair of theoretical physics at the University of Vienna in 1894. His decision to return to Vienna may well have been influenced significantly by his worsening myopia and the generous retirement package offered by the University of Vienna as compared to that offered by the University of Munich.

Boltzmann's decision to accept the chair of theoretical physics in Vienna turned out to be a mistake. Munich was a hotbed of physical research, while his hometown Vienna was much less so. Moreover, Vienna soon harbored a philosophical climate that was strongly dominated by the phenomenological empiricism of Ernst Mach (1838–1916), which was violently hostile to Boltzmann's atomism, the core of his lifework. Mach moved to Vienna in 1895, the year after Boltzmann's return, to become Professor of Philosophy with Special Emphasis on the History and Theory of the Inductive Sciences.<sup>28</sup> Subsequently, both Boltzmann and Mach now performed on the same stage and competed for attention at the University of Vienna and at the Imperial Academy of Sciences. However, despite their fundamental scientific opposition and deep philosophical and epistemological differences (Mach's “dialectic rationalism”,<sup>29</sup> Boltzmann's “philosophical materialism”), they were on cordial personal terms and had the highest esteem for each other. Moreover, along with the classical philologist Theodor Gomperz (1832–1912) and his son, the philosopher Heinrich Gomperz (1873–1942), Boltzmann supported Mach's call to Vienna.<sup>30</sup> There is no justification whatever for the enduring

<sup>27</sup> “Ärztliches Gutachten über den nervlichen Zustand Boltzmanns, Graz, den 24. Juni 1888”, in Herbert Hörz and Andreas Laass, *Ludwig Boltzmanns Wege nach Berlin – Ein Kapitel österreichisch-deutscher Wissenschaftsbeziehungen* (Berlin: Akademie-Verlag, 1989), pp. 109–110; reproduced in facsimile in Abb. 10a)–c). The term neurasthenia has been coined by the American physician and neurologist George Miller Beard (1839–1883) in the year 1869. Using today's terminology, Boltzmann probably was in a depressive phase of a cyclothymic disorder.

<sup>28</sup> In German: Ordentlicher Professor der Philosophie, insbesondere für Geschichte und Theorie der induktiven Wissenschaften.

<sup>29</sup> Paul K. Feyerabend, “Machs Theorie der Forschung und ihre Beziehung zu Einstein”, in Rudolf Haller and Friedrich Stadler, ed., *Ernst Mach – Werk und Wirkung* (Wien: Verlag Hölder-Pichler-Tempsky, 1988), pp. 435–462; especially pp. 448–458.

<sup>30</sup> Heinrich Gomperz, “Ernst Mach”, *Archiv für Geschichte der Philosophie* 29 (1916), 325–326; John T. Blackmore, *Ernst Mach: His Work, Life, and Influence* (Berkeley, Los Angeles, London: University of California Press, 1972), pp. 145–163; “[Machs] Briefwechsel mit Theodor Gomperz”, in Haller and Stadler,

myth, which still circulates among physicists and others,<sup>31</sup> that Mach's rejection of Boltzmann's atomism led to Boltzmann's tragic end.

Boltzmann remained in Vienna only six years before moving to the University of Leipzig as Professor of Theoretical Physics in 1900, a decision he initially embraced owing to the less-than-satisfactory circumstances that had developed in his institute in Vienna. Thus, he complained that he was a mere "schoolmaster" in Vienna; that his students, who were mainly candidates for teaching positions in secondary schools (*Gymnasia*), lacked interest in physics; and that the lively scientific atmosphere he had experienced in Munich was strikingly absent in Vienna. The physical chemist Wilhelm Ostwald (1853–1932), the most energetic "energetist" of the period and close adherent to Mach's philosophy, paved the way for Boltzmann's call to Leipzig, which Boltzmann prized as an outstanding instance of scientific enmity being compatible with personal friendship. Nevertheless, Boltzmann's move to Leipzig was a disaster: During the summer prior to leaving Vienna, he had a nervous breakdown, for which he had to be hospitalized in a sanatorium, and even though he was welcomed with open arms by the Leipzig faculty after his release, his depression was so severe that he made the first attempt on his own life in Leipzig. In contrast to his usual outspokenness, he never talked to anyone later about the two years he spent in Leipzig. In Vienna, his chair had remained vacant, probably because he already had begun to negotiate his return before leaving for Leipzig.

## The philosopher-scientist

Although Boltzmann's writings on the philosophy of science and epistemology belong to his lesser-known and little-discussed legacy, he made important contributions to this field, presenting a theory of scientific change that was inspired by Darwin's theory of evolution. He even speculated on an extension of physical theory to biology, recognising that there is no contradiction between biological evolution and the laws of thermodynamics.<sup>32</sup> For the famous 10th (1902) edition of the *Encyclopaedia Britannica* Boltzmann wrote an article on "Model", extending his earlier writings on pictures.<sup>33</sup>

**In defense of atomism.** Around the time when Boltzmann moved to Leipzig, both the concept and the consistency of atomism were challenged on physical as well as philosophical grounds. The reversibility and recurrence paradoxes and the problem of specific heat weakened the credibility of atomistic theories. Moreover, Boltzmann's

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*Ernst Mach* (ref. 28), pp. 213–228.

<sup>31</sup> See, for example, Lewis S. Feuer, *Einstein and the Generations of Science* (New York: Basic Books, 1974), pp. 335–341.

<sup>32</sup> Stephen G. Brush, *Ludwig Boltzmann and the Foundation of Natural Science*. in Ilse Maria Fasold-Boltzmann and Gerhard Ludwig Fasold, ed., *Ludwig Boltzmann (1844–1906). Zum hundertsten Todestag* (Wien, New York: Springer-Verlag, 2006), pp. 65–80; on p. 80.

<sup>33</sup> Ludwig Boltzmann, *Model*. Encyclopaedia Britannica. Vol. XXX, pp. 788–791, (London: "The Times" Printing House, 1902); reprinted in: Cambridge University Press, 11th edition, 1911; Brian McGuinness (ed.), (ref. 36), pp. 211–220.

atomism was put into question by the “energetics” doctrines represented by Ostwald and the theoretical physicist Georg Helm (1851–1923) from Dresden, with Mach in the background as their somewhat reluctant godfather regarding “energetics”. The energetists’ positivistic view and phenomenological (Machian) epistemology discarding atomism had their complement in Pierre Duhem’s (1861–1916) positivistic approach of thermodynamics. Furthermore, Henri Poincaré (1854–1912) was not a keen supporter of atomism. So, during the last decade of the 19th century the scientific community of continental Europe with Germany and France leading, turned away from atomism and philosophical materialism in favour of phenomenological and positivistic approaches. The support of the kinetic theory and atomism was restricted to supporters in England and the Netherlands.

At the 67. *Versammlung der Gesellschaft der Deutschen Naturforscher und Ärzte* in Lübeck in September 1895 Ostwald, Helm and Boltzmann used the opportunity to bring their arguments before the German scientific community.<sup>34</sup> Boltzmann most successfully fought for atomism and the kinetic theory during a two-day debate with Ostwald and Helm and he inspired a younger generation of physicist, among them Max Planck (1858–1947) and Arnold Sommerfeld (1868–1951). Boltzmann, the “bullish” defender of his standpoint (so Sommerfeld in his often cited report on the fierce debate),<sup>35</sup> was not a philosophical doctrinist but rather flexible when he was reflecting on the construction of representations (models) or pictures (“Bilder”). In that respect, Boltzmann was critically following Heinrich Hertz (1857–1894) and his conception of pictures presented in the preface of his *Principles of Mechanics*.<sup>36</sup> Although we have no direct (written) evidence by Boltzmann himself it seems to be plausible to assume that he already had been acquainted with the notion of mental pictures or representations much earlier through the work of Robert von Zimmermann (1824–1898) and his textbook *Philosophische Propaedeutik*.<sup>37</sup> Boltzmann studied philosophy with Zimmermann who became professor at the University of Vienna in 1861.

<sup>34</sup> Walter Höflechner, *Ludwig Boltzmann: Leben und Briefe* (Graz: Akademische Druck- u. Verlagsanstalt, 1994), pp. I 164–171. Erhard Scheibe, *Die Philosophie der Physiker* (München: C. H. Beck, 2006), pp. 104–119. Christa Jungnickel and Russell McCormack, *Intellectual Mastery of Nature. Theoretical Physics from Ohm to Einstein*. Vol. 2. The Now Mighty Theoretical Physics 1870–1925. (Chicago and London: The University of Chicago Press, 1986), pp. 217–227.

<sup>35</sup> “Das Referat für die Energetik hatte Helm - Dresden; hinter ihm stand Wilhelm Ostwald, hinter beiden die Naturphilosophie des nicht anwesenden Ernst Mach. Der Opponent war Boltzmann, sekundiert von Felix Klein. Der Kampf zwischen Boltzmann und Ostwald glich, äußerlich und innerlich, dem Kampf des Stieres mit dem geschmeidigen Fechter. Aber der Stier besiegte diesmal den Torero trotz all seiner Fechtkunst. Die Argumente Boltzmanns schlugen durch. Wir damals jüngeren Mathematiker standen auf der Seite Boltzmanns; es war uns ohne weiters einleuchtend, dass aus der einen Energiegleichung unmöglich die Bewegungsgleichungen auch nur eines Massenpunktes, geschweige denn eines Systems von beliebigen Freiheitsgraden gefolgt werden könnten”. Arnold Sommerfeld, *Das Werk Boltzmanns*. Lecture at the occasion of Ludwig Boltzmann’s 100th birthday. Quoted in Erhard Scheibe, *Die Philosophie der Physiker*. (ref. 33), pp. 105–106.

<sup>36</sup> Heinrich Hertz, *Die Prinzipien der Mechanik in neuem Zusammenhange dargestellt*. Gesammelte Werke, Band III. (Leipzig: Johann Ambrosius Barth, 1894), pp. 1–5; reprinted in Ostwalds Klassiker Vol. 263 (Frankfurt am Main: Verlag Harri Deutsch, 2. Auflage 1996.)

<sup>37</sup> Robert Zimmermann, *Philosophische Propaedeutik*. (Wien: Wilhelm Braumüller, 1852, 2nd ed. 1860, 3rd ed. 1867.) See also Andrew D. Wilson, “Hertz, Boltzmann and Wittgenstein Reconsidered”, *Studies in History and Philosophy of Science* 20 (1989), No. 2, 245–263.

**Hertz – Darwin – Mach.** Boltzmann admired the work of Hertz but had a different view on the relation of the concept of reality and reality proper. Boltzmann criticised the existence of *a priori* valid laws of logic or knowledge, or explanations independent of our experience. Following Charles Darwin (1809–1882) Boltzmann's evolutionist conception of epistemology did not allow for such laws of knowledge.

*What then will be the position of the so-called laws of thought in logic?  
Well, in the light of Darwin's theory they will be nothing else but inherited  
habits of thought.<sup>38</sup>*

This passage in his polemics against Schopenhauer of 1905 sounds like the programmatic statement of one of the followers of evolutionary epistemology in the eighties of the last century. Darwin was a strong ally for his mechanistic, i.e. materialistic world view:

*In my view all salvation for philosophy may be expected to come from  
Darwin's theory. As long as people believe in a special spirit that can  
cognize objects without mechanical means, or in a special will that likewise  
is apt to will that which is beneficial to us, the simplest psychological  
phenomena defy explanation.*

*Only when one admits that spirit and will are not something over and  
above the body but rather the complicated action of material parts whose  
ability so to act becomes increasingly perfected by development, only when  
one admits that intuition, will and self-consciousness are merely the high-  
est stages of development of those physico-chemical forces of matter by  
which primeval protoplasmic bubbles were enabled to seek regions that  
were more and avoid those that were less favourable for them, only then  
does everything become clear in psychology.<sup>39</sup>*

For Boltzmann strong philosophical convictions, like Hertz' apriorism or Mach's phenomenology, were of little use in physics. Boltzmann in a very pragmatic way was led by the power of physical models of explanation (his "Bilder") justified by mathematical consistency. What Boltzmann probably had in mind when he was referring to pictures or models was an "isomorphism" between the structural elements of a physical proposition and the attributed mathematical elements but strongly guided (or modeled) by pictures or visualizable representations. Opposing Mach's epistemological anti-realism and empiricism Boltzmann's position was that of a realist. But his epistemological realism was not a naive realism equating physical models ("Bilder") with direct representations of reality. One even is tempted to find traits of an instrumentalism in Boltzmann's writings

<sup>38</sup>Ludwig Boltzmann, "Eine These Schopenhauers". in *Populäre Schriften*. (ref. 10), pp. 385–402; eingeleitet und ausgewählt von Engelbert Broda (Braunschweig und Wiesbaden: Friedr. Vieweg & Sohn, 1979), pp. 240–257, on page 252; translated into English in Brian McGuinness (ed.), *Ludwig Boltzmann. Theoretical Physics and Philosophical Problems. Selected Writings* (Dordrecht: Reidel, 1974), pp. 185–198, on page 194.

<sup>39</sup>ibid., in *Populäre Schriften*. (ref. 10), pp. 385–402; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 240–257, on page 251; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 185–198, on page 193.

when he presents the atomistic hypothesis as the most convincing and comprehensive, simple and elegant description of the natural phenomena.

In his lecture on the “*Development of methods of theoretical physics*” delivered at the 71. *Versammlung der Gesellschaft der Deutschen Naturforscher und Ärzte* in Munich in September 1899 Boltzmann remarks:

[...] namely that no theory can be objective, actually coinciding with nature, but rather that each theory is only a mental picture of phenomena, related to them as sign is to designatum. From this it follows that it cannot be our task to find an absolutely correct theory but rather a picture that is, as simple as possible and that represents phenomena as accurately as possible.<sup>40</sup>

And he concluded:

*The question whether matter consists of atoms or is continuous reduces to the much clearer one, whether [the conception of enormously many individuals or that of] the continuum is able to furnish a better picture of phenomena.*<sup>41</sup>

Moreover, Boltzmann’s ontological position regarding atoms was flexible and he repeatedly made clear that he preferred an open and pragmatic attitude. In his discussion on the identity of psychic processes with certain material processes in the brain Boltzmann adds a most remarkable footnote:

*That is, if the concept of continuum is properly understood, an interplay of its atoms, by which of course we must not imagine material points but perhaps vectors or whatever. Nor do the atoms necessarily have to be immutable.*<sup>42</sup>

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<sup>40</sup> “[...] dass keine Theorie etwas Objektives, mit der Natur wirklich sich Deckendes sein kann, dass vielmehr jede nur ein geistiges Bild der Erscheinung ist, das sich zu diesem verhält, wie das Zeichen zum Bezeichneten. Daraus folgt, dass es nicht unsere Aufgabe sein kann, eine absolut richtige Theorie, sondern vielmehr ein möglichst einfaches, die Erscheinungen möglichst gut darstellendes Abbild zu finden”. Ludwig Boltzmann, “Über die Entwicklung der Methoden der theoretischen Physik in neuerer Zeit”, in *Populäre Schriften*. (ref. 10), pp. 198–277; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 120–149, on page 137; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 77–100, on page 90.

<sup>41</sup> “Die Frage, ob die Materie atomistisch zusammengesetzt oder ein Kontinuum ist, reduziert sich auf die viel klarere, ob die Vorstellung enorm vieler Einzelwesen oder die eines Kontinuums ein besseres Bild der Erscheinungen zu liefern vermöge”. Ludwig Boltzmann, “Über die Entwicklung der Methoden der theoretischen Physik in neuerer Zeit”, in *Populäre Schriften*. (ref. 10), pp. 198–277; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 120–149, on page 138; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 77–100, on page 91. Insertion in brackets [...] is added by the author.

<sup>42</sup> “D. h. bei richtiger Auffassung des Begriffs des Kontinuums ein Spiel der Atome desselben, worunter man sich freilich nicht materielle Punkte denken muss, sondern vielleicht Vektoren oder wer weiß was. Auch müssen die Atome nicht notwendig unveränderlich sein”. Ludwig Boltzmann, “Über die Frage nach der objektiven Existenz der Vorgänge in der unbelebten Natur”, in *Populäre Schriften*. (ref. 10), pp. 162–187; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 94–119, on page 112; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 57–76, on page 76.

Theories of the continuum had been regarded in Boltzmann's times as phenomenological theories in opposition to atomistic theories and hence atomism was not a phenomenological theory. What Boltzmann is telling us here in defence of atoms is the fact that continuum mechanics – if “properly understood” – also has to go beyond pure phenomenology by assuming its own “atoms”, “perhaps vectors or whatever”. On the methodological level Boltzmann's mechanical atom is represented by a picture (“Bild”) central to his mechanistic (realistic) world view. On the epistemological level he is cautious enough not to identify his mechanical atoms with the real world out there.

*Über die Beschaffenheit der Atome aber wissen wir noch gar nichts und werden auch solange nichts wissen, bis es uns gelingt, aus den durch die Sinne beobachtbaren Tatsachen eine Hypothese zu formen.*<sup>43</sup>

And he prophetically remarks in this essay of 1886:

*Merkwürdigerweise ist hier am ersten wieder von der Kunst Erfolg zu hoffen, welche sich auch bei Erforschung der Himmelskörper so mächtig erwies, von der Spektralanalyse.*<sup>44</sup>

**New physics.** His farsighted consideration of spectral analysis as a powerful tool to reveal the inner structure of atoms, “...die Beschaffenheit der Atome...”, of 1886 is in sharp contrast to the observation that he never mentioned the phenomena of radioactivity discovered twelve years later. This is puzzling because as a member of the Vienna Academy of Sciences he was well informed about the seminal role Vienna played in fostering radioactivity research in Paris in supplying the Curies in 1898–99 with more than one ton of pitchblend residues from the then Austrian uranium mine in St. Joachimsthal (now Jáchimov, Czech Republic), which enabled Marie Curie (1867–1934) and Pierre Curie (1859–1906) to discover polonium and radium. Moreover, with their work in 1899, Stefan Meyer (1872–1949) and Egon von Schweidler (1873–1948), both Boltzmann's students at the Vienna institute, correctly distinguished between the radiation from radium ( $\alpha$ -rays) and from polonium ( $\beta$ -rays) by their different behaviour in a magnetic field. (The electromagnet had been available at Boltzmann's institute.) They proved that the deflection of the radium rays was identical to that of cathode rays, that is, that the radium rays consist of negatively charged particles. This led to the fundamental insight of the corpuscular nature of these rays which is strong experimental support of the atomistic nature of these new phenomena.<sup>45</sup> Although Boltzmann wrote

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<sup>43</sup>Ludwig Boltzmann, “Der zweite Hauptsatz der mechanischen Wärmetheorie”, in *Populäre Schriften*. (ref. 10), pp. 25–50, on p. 30; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 26–46, on page 31; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 5713–32, on page 17; here the translation is highly misleading.

<sup>44</sup>Ibid., the passage cited here in German is missing in the English translation.

<sup>45</sup>St. Meyer and E. v. Schweidler, “Über das Verhalten von Radium und Polonium im magnetischen Felde”, *Anzeiger der kaiserl. Akad. d. Wiss., mathem.-naturw. Kl.* 22 (November 3, 1899), 1–4. St. Meyer and E. v. Schweidler, “Über das Verhalten von Radium und Polonium im magnetischen Felde. (I. Mitteilung)”, *Physikalische Zeitschrift* 1 (1899), 90–91. St. Meyer and E. v. Schweidler, “Weitere Notizen über das Verhalten von Radium im magnetischen Felde”, *Anzeiger der kaiserl. Akad. d. Wiss., mathem.-naturw. Kl.* 23

a popular account on *X*-rays a few month after their discovery by Konrad Röntgen (1854–1923),<sup>46</sup> he never mentioned the ongoing work on radioactivity research at his own institute. Probably he took notice of the recent developments and just did not comment on them, but it seems more likely that he had lost interest in actual physical research during his last years. In his *Lectures on Natural Philosophy* 1903–1906 he did not present anything referring to new physics. During the last decade of his life he no longer contributed to the forefront of research but commented on what he had achieved and tried to secure his work in writing monographs and popular articles.

Throughout his life Boltzmann was very interested in technology. He considered technological progress as a confirmation of the sciences.

*That is why I do not regard technological achievements as unimportant by-products of natural science but as a logical proof. Had we not attained these practical achievements, we should not know how to infer. Only those inferences are correct that lead to practical success.*<sup>47</sup>

In fact Boltzmann argues here as a scientific realist (and atomist) implicitly against idealism (and phenomenological anti-atomism) in taking the progress of science (and technology) as a confirmation of his epistemological position – realism. So, the growing experience and the accumulation of increasingly refined knowledge produced by science (and applied by technology) corroborate realism. Despite of Boltzmann's strong anti-metaphysical sentiments his own concept of realism is part of a metaphysical concept. Probably, Boltzmann was quite aware of that fact and therefore disguised his epistemological realism as a methodological principle, in sharp contrast to Mach's concept. What I mean by disguising realism is Boltzmann's view of the conception of pictures (“Bilder”) as representations of the “world out there”. Admittedly, since Boltzmann never has developed his philosophy of science in a systematic manner, his ideas are a profound source of various interpretations and misunderstandings.

What makes reading his *Populäre Schriften* such a delightful experience is Boltzmann's humour. In a slightly poetic manner Boltzmann speaks about the power of theory.

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(November 9, 1899), 1–2. St. Meyer and E. v. Schweidler, “Über das Verhalten von Radium und Polonium im magnetischen Felde. (II. Mitteilung)”, *Physikalische Zeitschrift* 1 (1899), 113–114. F.O. Giesel, “Über die Ablenckbarkeit der Becquerelstrahlen im magnetischen Felde”, *Annalen der Physik* 69 (1899), 834–836. J. Elster und H. Geitel, “Über den Einfluss eines magnetischen Feldes auf die durch die Becquerelstrahlen bewirkte Leitfähigkeit der Luft”, *Verhandlungen der Deutschen Physikalischen Gesellschaft* 1 (1899), 136–138 (Sitzung von 5. Mai 1899). H. Becquerel, “Déviation du rayonnement du radium dans un champ électrique”, *Comptes Rendus* 130 (1900), 809; cf. also E. Rutherford, *Radioactive Transformations* (New Haven: Yale University Press, 1906), p. 9. For the history of early experiments of the deflection of Becquerel radiation, see Marjorie Malley, “The Discovery of the Beta Particle”, *American Journal of Physics* 39 (1971), 1454–1461.

<sup>46</sup> Ludwig Boltzmann, “Röntgens neue Strahlen” in *Populäre Schriften*, (ref. 10), pp. 188–197.

<sup>47</sup> “Deshalb halte ich die Errungenschaften der Technik nicht für nebensächliche Abfälle der Naturwissenschaften, ich halte sie für logische Beweise. Hätten wir diese praktischen Errungenschaften nicht erzielt, so wüssten wir nicht, wie man schliessen muss. Nur solche Schlüsse, welche praktischen Erfolg haben, sind richtig.“ Ludwig Boltzmann, “Eine These Schopenhauers”, in *Populäre Schriften*, (ref. 10), pp. 385–402; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 240–257, on page 249; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 185–198, on page 193.

*The gigantic structures of the Brooklyn Bridge that stretches beyond sight and the Eiffel tower that soars without end rest not only on the solid framework of wrought iron, but on the solider one of elasticity theory.*<sup>48</sup>

In 1894, at the 66. *Versammlung der Gesellschaft der Deutschen Naturforscher und Ärzte* in Vienna he gave a lecture “On Airship Flight” (“Über Luftschiffahrt”), on flying objects heavier than air by demonstrating models of aeroplanes of the Austrian aeronautics pioneer Wilhelm Kress (1836–1913) which Boltzmann let fly around in the congregation hall of the assembly at the Vienna Musikverein.<sup>49</sup> Boltzmann was correct in his clear-sighted prediction that not airships but aeroplanes would be the superior technology of the future.

## Boltzmann’s last years, 1902–1906

Ever since his aborted move to Berlin in 1888, Boltzmann had become increasingly trapped in self-conflict regarding his recurrent wish to change universities. He moved back to Vienna in 1902, but as a condition of his appointment had to promise in writing never to leave Austria again: Emperor Franz Joseph I, who was not a particularly dedicated supporter of the sciences, was not amused by the peregrinations of his famous but unreliable subject. Further disruption followed: Because of the urgent need for more space for the Institute of Physics, now at Türkenstrasse 3 in the IX District, the University of Vienna appropriated the apartment in it where the Boltzmann family was living. This was Boltzmann’s official university residence, and to compensate him for its loss the Ministry for Education (*Ministerium für Cultus und Unterricht*) gave him a sum of money with which he bought a villa at Haizingergasse 26 in the XVIII District (Währing), which is still owned by his descendants. Not far from Boltzmann’s house, at Haizingergasse 29, Theodor Herzl (1860–1904) spent his last years. We have no evidence that the two great men took notice of each other.

Boltzmann now lectured on theoretical physics at the University of Vienna and finished the second volume of his *Lectures on the Principles of Mechanics*.<sup>50</sup> In 1904, on the occasion of his 60th birthday, he was presented with a splendid Festschrift that was edited by his assistant Stefan Meyer and comprised 117 contributions from the international community of physicists.<sup>51</sup> Despite this universal acclaim, however,

<sup>48</sup>Der Riesenbau der Brooklyner Brücke, welche sich unabsehbar in die Länge, und der des Eifelturms, der sich endlos in die Höhe erstreckt, sie beruhen nicht bloss auf dem festen Gefüge des Schmiedeeisens, sondern auf dem festeren der Elastizitätstheorie. Ludwig Boltzmann, “Über die Bedeutung von Theorien”, in *Populäre Schriften*, (ref. 10), pp. 76–80; eingeleitet und ausgewählt von Engelbert Broda (ref. 36), pp. 54–58, on page 56; translated into English in Brian McGuinness (ed.), (ref. 36), pp. 33–36, on page 35.

<sup>49</sup>Ludwig Boltzmann, “Über Luftschiffahrt”, in *Populäre Schriften* (ref. 10), pp. 81–91. As a mere curiosity I note, that Ludwig Wittgenstein (1889–1951) who considered Boltzmann’s philosophical writings as an important influence on his own thinking first studied mechanical engineering at the Technische Hochschule in Charlottenburg, Berlin for two years before he went to Manchester where he studied aeronautics.

<sup>50</sup>Idem, *Vorlesungen über die Prinzipien der Mechanik*. 2 Vols. (Leipzig: Johann Ambrosius Barth, 1897, 1904).

<sup>51</sup>Stefan Meyer, ed., *Festschrift Ludwig Boltzmann gewidmet zum sechzigsten Geburtstage 20. Februar 1904* (Leipzig: Johann Ambrosius Barth, 1904).

Boltzmann's wife sent an alarming message to their daughter Ida (1884–1910), who had remained in Leipzig to finish school: “*Daddy gets worse every day. He has lost his faith in our future. I had imagined a better life here in Vienna*”.<sup>52</sup> Boltzmann suffered from heavy attacks of asthma and headaches, and he was nearly blind from his myopia. He also had undertaken an additional heavy burden after Mach suffered a stroke in 1898 and retired from his chair at the University of Vienna in 1901: He took over Mach's lecture course on the philosophy and methodology of science (*Philosophie der Natur und Methodologie der Naturwissenschaften*) in 1903. He began it with great success, but after a few lectures was unable to continue.<sup>53</sup> This further undermined his self-confidence.

Despite his increasing physical and mental disabilities, he crossed the Atlantic twice, in 1904 and 1905. (He had done so once before when he had lectured at Clark University in Worcester, Massachusetts, in 1899.) In 1904 he gave an invited lecture in St. Louis, Missouri, in connection with the World Fair,<sup>54</sup> and in 1905 he lectured at the University of California in Berkeley and at Stanford University. Boltzmann memorialized his trip to California in a typically humorous essay, “*Journey of a German Professor to Eldorado*”, which was published in his *Popular Writings* and remains a delightful piece of prose.<sup>55</sup>

That was Boltzmann's last burst of intellectual activity; it was followed by a deep depression and hospitalization. He gave his last course on theoretical physics at the University of Vienna in the winter semester of 1905–1906; subsequently, he was unable to fulfil his teaching duties in the summer semester of 1906 owing to his physical and mental suffering. His mental condition was officially diagnosed as a serious form of neurasthenia, a vaguely defined term denoting a general weakness of the nervous system associated with a broad spectrum of mental disorders ranging from anxiety to sleeplessness.<sup>56</sup> In light of his symptoms, however, it is likely that Boltzmann was suffering from a much more serious mental illness: manic depression.

**Death in Duino.** Ludwig Boltzmann took his own life at one of the most scenic spots on the Adriatic coast, in Duino, near Trieste, a little village that is overlooked by an old castle in the possession of the noble family della Torre e Tasso where the Austrian poet Rainer Maria Rilke (1875–1926), as poet in residence, began to compose his famous

<sup>52</sup> Quoted in Cercignani, *Ludwig Boltzmann* (ref. 10), p. 30.

<sup>53</sup> Fasol-Boltzmann, *Ludwig Boltzmann* (ref. 15). For valuable new biographical material, see Ilse Maria Fasold-Boltzmann and Gerhard Ludwig Fasold, ed., (ref. 31).

<sup>54</sup> Ludwig Boltzmann, “The Relations of Applied Mathematics”, in Howard J. Rogers, ed., *Congress of Arts and Science Universal Exposition, St. Louis, 1904*. Vol. IV. *Physics Chemistry Astronomy Sciences of the Earth* (Boston and New York: Houghton, Mifflin, 1906), pp. 591–603; reprinted in Katherine R. Sopka, ed., *Physics for a New Century: Papers Presented at the 1904 St. Louis Congress* (New York: Tomash Publishers and American Institute of Physics, 1986), pp. 267–279.

<sup>55</sup> Idem, “Reise eines deutschen Professors ins Eldorado”, in *Populäre Schriften*. (ref. 10), pp. 403–435; eingeleitet und ausgewählt von Engelbert Broda (Braunschweig und Wiesbaden: Friedr. Vieweg & Sohn, 1979), pp. 258–290; reprinted in Dieter Flamm, ed., (ref. 19), pp. 235–256; translated into English in *Transport Theory and Statistical Physics* **20** (December 1991), 499–523, *Physics Today* **45** (January 1992), 44–51, and Carlo Cercignani, (ref. 10), pp. 231–250.

<sup>56</sup> Eugen Bleuler, *Lehrbuch der Psychiatrie*, 14. Auflage, neubearbeitet von Manfred Bleuler (Berlin, Heidelberg, New York: Springer-Verlag, 1979), pp. 519–522.

*Duino Elegies* six years later. The Viennese newspaper *Die Zeit* reported the tragic news on Friday, September 7, 1906: “He hanged himself with a short cord from the crossbar of a window casement. His daughter was the first to discover the suicide”.<sup>57</sup>

The Boltzmanns had planned to return to Vienna on Thursday, September 6. The day before, his wife Henriette and their youngest daughter Elsa (1891–1965) went for a swim, expecting Boltzmann to join them, but he never did. He had relapsed into that black state of mind that had tormented him for years. Despite the relaxed atmosphere during this late-summer family holiday by the sea, which he had long promised to spend with his beloved wife, he was restless and deeply depressed. Increasingly shortsighted, anxious about his ability to carry out his teaching duties at the University of Vienna for the forthcoming semester, and beset by the manic depression that had led earlier to more than one hospitalization, Boltzmann committed suicide on September 5, 1906, in his room in the Hotel Ples,<sup>58</sup> which today is part of the international United World College of the Adriatic – Collegio del Mondo Unito dell’ Adriatico. His daughter Elsa had been sent back to the hotel by her mother to check up on her father and thus was the first person to discover the tragedy, a gruesome and shocking experience that she never talked about for the rest of her life.

Boltzmann passed from this world without leaving a suicide note, but the preface to his lectures on mechanics, which Boltzmann signed in the Austrian resort town of Abbazia (today Opatija, Croatia) on August 3, 1897, opens with a motto that he carefully chose to sum up his view of science and of life:<sup>59</sup>

<i>Bring' vor, was wahr ist; Schreib' so, dass es klar ist Und verficht's, bis es mit dir gar ist!</i>	(Put forward what is true; So write that it's clear And fight for it to the end!)
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Boltzmann’s funeral took place on Saturday, September 8, 1906, at the Döbling cemetery in the XIX District of Vienna at the unusually late hour of seven o’clock in

<sup>57</sup> “Aus Triest kommt uns die Meldung: Hofrat Prof. Dr. Ludwig Boltzmann, der zum Sommeraufenthalt mit seiner Tochter in Duino weilte, wurde gestern als Leiche in seinem Zimmer aufgefunden. Er hatte sich mit einem kurzen Strick am Fensterkreuz erhängt. Seine Tochter war die erste, die den Selbstmord entdeckte”. “Wiener Neuigkeiten. Selbstmord des Prof. Boltzmann”, *Die Zeit*, No. 1420 (September 7, 1906), p. 1.

<sup>58</sup> Several locations have been advanced for where Boltzmann committed suicide. Boltzmann’s colleague in Vienna, the mathematician Franz Mertens (1840–1927), claimed that it was in the church of Duino, but this claim can be excluded, because the church was never reconsecrated; see Walter Höflechner, *Ludwig Boltzmann: Leben und Briefe*, (ref. 33), p. I 289. That Boltzmann committed suicide in his hotel room is supported by a short obituary, “Die Ausführung des Selbstmords”, in the Viennese *Neue Freie Presse*, No. 15102 (September 7, 1906), p. 3, but the hotel is not named in it. The name of the hotel, the Hotel Ples, is given in a short note in the Slovenian newspaper, *Edinost*, No. 247 (September 7, 1906), p. 2. This was published by Martin Breclj in the Slovenian daily, *Primorski Dnevnik*, No. 83 (April 9, 2006), p. 12, under the title, “Pred sto leti je v Devinu umrl veliki avstrijski fizik Ludwig Edward Boltzmann [A hundred years ago the great Austrian physicist Ludwig Eduard Boltzmann died in Duino]”. Further confirmation of the hotel’s name and of its address, Duino 50/54, is found in the parish register, *Liber Defunctorum* (Book of the Dead), of the Catholic Parish Church of Duino together with the cause of his death. Under the heading, *Morbus seu Causa Mortis* (Illness or cause of death), we read *Suicidium alienatione mentali se suspenso perpetravit* (He committed suicide in a state of mental alienation by hanging himself). A plaque in memory of Ludwig Boltzmann was mounted on the Hotel Ples in Duino on September 4, 2006.

<sup>59</sup> Boltzmann, *Vorlesungen über die Prinzipien der Mechanik*. Vol. 1 (ref. 49), p. v.

the evening. The train from Trieste bearing Boltzmann's coffin had been delayed for hours by heavy weekend traffic. Boltzmann's assistant Stefan Meyer was the last of the mourners to speak at Boltzmann's open grave.<sup>60</sup> He closed his eulogy on behalf of Boltzmann's students with their teacher's battle cry: "*Reinheit und Klarheit im Kampf um die Wahrheit!*" (Purity and Clarity in the Struggle for Truth!)<sup>61</sup>

## Boltzmann's legacy

At the center of Boltzmann's lifelong struggles in physics and philosophy was the question of the reality of atoms. In the 1870s, when Boltzmann was at the zenith of his intellectual powers, there was no conclusive experimental evidence for the existence of atoms. He had to fight his lonely battle on two fronts: for his belief in the reality of atoms against Mach and the empiricists, and for his statistical interpretation of the second law of thermodynamics, his most revolutionary and lasting contribution to physics, against Loschmidt and others. Boltzmann's struggle on these two fronts was ironic in retrospect, as pointed out by Leo P. Kadanoff:

*Mach was wrong about atoms and wrong in demanding that science only include the immediately visible, but right in demanding a different philosophic outlook for kinetic theory. Boltzmann was right about atoms but utterly wrong in believing that atoms provided a necessary basis for thermodynamics. The second law does not require atoms.*<sup>62</sup>

Thermodynamics, in other words, is neutral with respect to models of the microphysical world.

Boltzmann's goal of translating the behavior of the physical world into rigorously defined mathematical entities that obey well-defined rules remains an open game today, one that is still centered upon the second law of thermodynamics, a law that Einstein regarded as an unshakeable and fundamental pillar of the physical world. As he wrote:

*A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamic made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (for the special attention of those who are skeptics on principle).*<sup>63</sup>

<sup>60</sup>For more on Stefan Meyer, see Wolfgang L. Reiter, "Stefan Meyer: Pioneer of Radioactivity", *Physics in Perspective* 3 (2001), 106–127.

<sup>61</sup>·Hofrat Prof. Boltzmann. Das Leichenbegängnis in Wien", *Die Zeit*, No. 1422 (September 9, 1906), p. 4; "Hofrat Prof. Boltzmann. Das Leichenbegägnis", *Neues Wiener Tagblatt*, No. 49 (September 9, 1906), pp. 6–7.

<sup>62</sup>Leo P. Kadanoff, "Boltzmann's Science, Irony and Achievement" [Review of David Lindley, *Boltzmann's Atom* (ref. 3)], *Science* 291 (March 30, 2001), pp. 2553–2554; on p. 2553.

<sup>63</sup>Albert Einstein, "Autobiographical Notes", in Paul Arthur Schilpp, ed., *Albert Einstein: Philosopher-Scientist* (Evanston, Ill.: The Library of Living Philosophers, 1949), p. 33.

As Elliott H. Lieb and Jakob Yngvason have remarked, to derive the second law from statistical mechanics is “a goal that has so far eluded the deepest thinkers”.<sup>64</sup> Their recent axiomatic approach has enabled them to formulate the second law in a way that is entirely free of the concept of atoms that was so dear to Boltzmann.<sup>65</sup>

We are thus left with a final irony: The statistical formulation of the entropy that is engraved on Boltzmann’s tombstone in Vienna can be defined unambiguously and measured with no reference whatsoever to the atomic structure of matter.<sup>66</sup> But this is a common occurrence in science: The conceptual framework in which the creator of a new scientific concept worked is usually transformed by his or her successors. Still, as Einstein also wrote, scientists work “in the faith that facts by themselves can and should yield scientific knowledge without free conceptual constriction”.<sup>67</sup> Physics involves more than producing a consistent mathematical formulation of Nature. Atoms do exist, and Boltzmann was their passionate prophet. He saw the promised land but died too early to enter it.

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<sup>64</sup> Elliott H. Lieb and Jakob Yngvason, “The Physics and Mathematics of the Second Law of Thermodynamics”, *Physics Reports* **310** (1999), pp. 1–96; on p. 5.

<sup>65</sup> Idem, “A Fresh Look at Entropy and the Second Law of Thermodynamics”, *Physics Today* **53** (April 2000), pp. 32–37; “Letters: Entropy Revisited, Gorilla and All”, *ibid.* (October 2000), pp. 11–12, 14, 106.

<sup>66</sup> “Boltzmann’s identification of entropy as the logarithm of the area of the energy surface (when suitably revised in quantum-mechanical language) was a crucial insight about many systems, but the reason that this quantity obeys the second law, and the reason for the existence of the second law, are different questions”. See Elliott H. Lieb, “What if Boltzmann had known about Quantum Mechanics”, this volume pp. 27–36, on p. 36.

<sup>67</sup> Einstein, “Autobiographical Notes” (ref. 62), p. 49.

# Chronology

- 1844 20th February Ludwig Eduard Boltzmann born in Vienna  
John Dalton dies
- 1845 Michael Faraday discovers diamagnetism and paramagnetism  
(concept of magnetic field)  
Georg Cantor and Wilhelm Röntgen born
- 1847 Hermann von Helmholtz “Über die Erhaltung der Kraft”
- 1848 “March Revolution” in Vienna
- 1850 Rudolf Clausius “Über die bewegende Kraft der Wärme”  
(first statement on the second law of thermodynamics)
- 1853 Wilhelm Ostwald born
- 1854 Boltzmann attends Akademisches Gymnasium in Linz  
Henri Poincaré born  
Bernhard Riemann founds non-Euclidian geometry
- 1855 Karl Friedrich Gauss dies
- 1857 Heinrich Hertz born  
Rudolf Clausius “Über die Art der Bewegung, welche wir Wärme nennen”  
(establishes his kinetic theory of heat)
- 1858 Max Planck born
- 1859 Charles Darwin “The Origin of Species”  
Pierre Curie born
- 1860 James Clerk Maxwell develops his law of velocity distribution of particles  
in a gas
- 1862 David Hilbert born
- 1863 July: Boltzmann passes the “Matura” in Linz  
Oktober: Boltzmann begins his studies of mathematics and physics at the  
University of Vienna
- 1864 James Clerk Maxwell “A dynamical theory of the electromagnetic field”  
(introduces Maxwell's equations)  
Walter Nernst born
- 1865 Boltzmann's first publication “Über die Bewegung der Electricität in  
krummen Flächen”  
Rudolf Clausius coins the term entropy  
Gregor Mendel publishes his laws of heredity  
Josef Loschmidt determines the size of molecules
- 1866 19th December: Boltzmann's “Promotion” (PhD), University of Vienna  
Boltzmann's second publication “Über die mechanische Bedeutung des  
zweiten Hauptsatzes der Wärmetheorie”  
Assistent at the k.k. Physikalisches Institut, University of Vienna  
(October 1866 to September 1869)

	Bernhard Riemann dies
	War between Austria and Prussia
1867	Michael Faraday dies
	Marie Skodowska-Curie born
1868	7th March: Boltzmann's "Habilitation" in Mathematical Physics; "Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Körpern" (generalisation of Maxwell's velocity distribution law, Boltzmann factor)
1869	17th July: Boltzmann appointed Professor for Mathematical Physics at the Karl-Franzens-Universität Graz
1870	Boltzmann cooperates with Bunsen and Kundt at the Physics Institute, University of Heidelberg
1871	Boltzmann cooperates with Helmholtz at the Physics Laboratories, Friedrich-Wilhelm-University Berlin (experimental confirmation of Maxwell's theory)
	Ernst Zermelo and Ernest Rutherford born
1872	Boltzmann "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen" ( $H$ -theorem, Boltzmann equation)
1873	Boltzmann appointed Professor for Mathematics at the University of Vienna
	James Clerk Maxwell "Electricity and Magnetism"
	Johannes Diderik Van der Waals develops his gas law
1876	17th July: Boltzmann marries Henriette von Aigentler in Graz
	Boltzmann appointed Professor for Physics at the Karl-Franzens-Universität Graz
1878/79	Boltzmann becomes Dean of the Philosophical Faculty of the Karl-Franzens-Universität Graz
	Birth of first child, Ludwig Hugo
1879	Albert Einstein born
	James Clerk Maxwell dies
	Josef Stefan discovers "Stefan–Boltzmann Law"
1880	Birth of second child, Henriette
1881	Birth of third child, Arthur Ludwig
1882	Charles Darwin dies
1884	Boltzmann "Über eine von Hrn. Bartoli entdeckte Beziehung der Wärmestrahlung zum zweiten Hauptsatz" (proof of the "Stefan–Boltzmann Law") "Über die Eigenschaften monozyklischer und anderer damit verwandter Systeme" (ergodicity)
	Birth of fourth child, Ida Katerina
1887	Gustav Robert Kirchhoff dies
1887/88	Boltzmann becomes Rector of the Karl-Franzens-Universität Graz
1888	Boltzmann is called to the Friedrich-Wilhelm-University Berlin as successor of Kirchhoff; March: appointed; June: refusal

- Heinrich Hertz detects electromagnetic waves
- 1889 Death of Boltzmann's son Ludwig Hugo
- Ludwig Wittgenstein born
- 1890 Boltzmann appointed Professor for Theoretical Physics at the Ludwig-Maximilian University Munich
- 1891 Birth of fifth child, Elsa
- 1893 Josef Stefan dies
- 1894 Boltzmann appointed Professor for Theoretical Physics at the University of Vienna
- Journey to Oxford, Doctor of Civil Law honoris causa
- Heinrich Hertz dies
- Hermann von Helmholtz dies
- 1895 Josef Loschmidt dies
- Wilhelm Röntgen discovers *X*-rays
- Sigmund Freud and Josef Breuer publish "Studien über Hysterie" (foundation of psychoanalysis)
- 1896 Antoine-Henri Becquerel discovers natural radioactivity
- 1897 Joseph John Thomson discovers the electron
- 1898 Marie and Pierre Curie discover Polonium and Radium
- 1899 20th July to 2nd August: Boltzmann's journey to Worcester, USA  
Doctor of Laws honoris causa
- David Hilbert publishes "Grundlagen der Geometrie"
- 1900 Boltzmann appointed Professor for Theoretical Physics at the University of Leipzig
- Max Planck formulates his quantum hypothesis
- 1902 Boltzmann appointed Professor for Theoretical Physics at the University of Vienna
- Josiah Willard Gibbs " Elementary principles in statistical mechanics"
- 1903 5th May: Boltzmann's additional teaching position in philosophy:  
"Philosophie der Natur und Methodologie der Naturwissenschaften"  
Josef Stefan dies
- Josiah Willard Gibbs dies
- 1904 21st August to 8th October: Boltzmann travels to St. Louis, Detroit, Chicago, Washington D.C.
- Ernest Rutherford and Frederic Soddy interpret radioactivity as decay of atomic nuclei
- 1905 11th June to 3rd August: Boltzmann's journey to Berkeley, USA
- Albert Einstein postulates the light quantum (March 17th), calculates the motion of molecules in a liquid (Brownian motion), first (June 30th) and second (September 27th) paper on special relativity
- 1906 5th September: Boltzmann commits suicide in Duino near Trieste



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Lectures in Mathematics  
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## Boltzmann's Legacy

Giovanni Gallavotti, Wolfgang L. Reiter, Jakob Yngvason, Editors

Ludwig Eduard Boltzmann (1844–1906) was an Austrian physicist famous for his founding contributions in the fields of statistical mechanics and statistical thermodynamics. He was one of the most important advocates for atomic theory when that scientific model was still highly controversial. To commemorate the 100<sup>th</sup> anniversary of his death in Duino, the International Symposium "Boltzmann's Legacy" was held at the Erwin Schrödinger International Institute for Mathematical Physics in June 2006.

This text covers a broad spectrum of topics ranging from equilibrium statistical and nonequilibrium statistical physics, ergodic theory and chaos to basic questions of biology and historical accounts of Boltzmann's work. Besides the lectures presented at the symposium the volume also contains contributions specially written for this occasion. The articles give a broad overview of Boltzmann's legacy to the sciences from the standpoint of some of present day's leading scholars in the field.

The book addresses students and researchers in mathematics, physics and the history of science.

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