Realizing Boltzmann's dream: computer simulations in modern statistical mechanics

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Abstract. Today, computer simulations belong to the most important and powerful theoretical tools for the investigation of statistical mechanical systems particularly in the field of condensed matter. Many simulation methods may directly, or indirectly, be traced back to ideas of Ludwig Boltzmann or are used to carry on the program he had envisioned. Using several illustrative examples, we discuss the role of computer simulation in modern statistical mechanics and, in particular, its relation to Boltzmann's legacy.

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 availiable 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, Boltzmanns 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 evidencing 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 may 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 Sec. 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 using simple models that can be thoroughly simulated and visualized. As an example we mention the Lorentz gas, which in in Sec. 3 is used to illustrate mixing in phase space and in Sec. 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-equilbrium 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 Ref. [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 Newtons 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[1] [15], in a paper from 1884 Boltzmann considers stationary statistical ensembles of many system 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 calles “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 appropriate for particular experiments were developed and applied to a wide variety of situations. Examples include simulations algorithms for the grand-canonical ensemble (μVT-ensemble), which describes systems with fixed volume V at temperature T in contact with a particle reservoir with chemical potential μ, 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 in the arsenal of the computer simulator. Such thermostats also play a particularly important role in the molecular dynamics sim-

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[1] Note that, here, Cercignani cites the wrong article. Boltzmann considers ensembles (and, in particular, the microcanonical and canonical ensembles) in Ref. [13] and not in Ref. [14] as asserted by Cercignani.

ulation of non-equilibrium steady states, which are discussed in more detail in Sec. 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 Fig. 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.

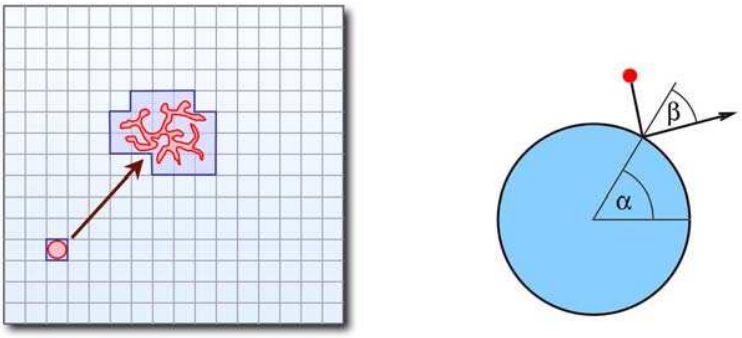

Figure 2. *Left panel:* Dispersion of a volume of initial conditions in phase space. *Right panel:* The Lorentz gas consists of a moving point particle that is elastically reflected when it collides with circular scatterers arranged on a regular triangular lattice. At the collision points, the state of the moving particle is specified by the two angles α and β.

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 Fig. 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 δ_0 in phase space diverge exponentially in time:

$$\delta_t \approx \delta_0 \exp(\lambda t). \tag{1}$$

Here, δ_t is the separation in phase space at time t and λ is called a Lyapunov exponent. This sensitivity to small perturbations of the initial conditions, which corresponds to a positive λ, 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 α and β which 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 occuring 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 Fig. 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 Fig. 3 and clearly demonstrate the spreading. Eventually, it leads to a uniform distribution over all of the available phase space.

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 Fig. 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

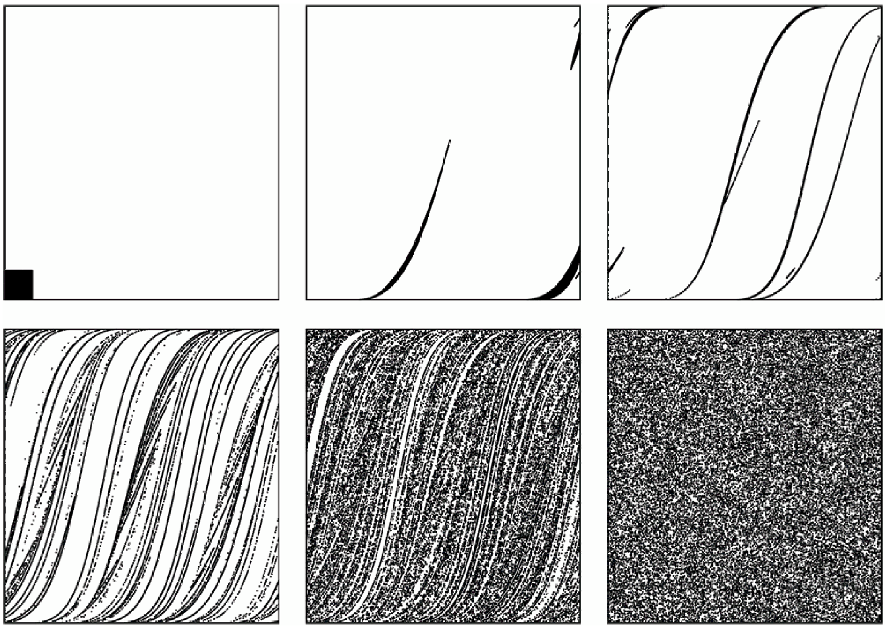

Figure 3. Spreading of initial conditions initially concentrated in a small part of phase space. Shown are sections of the phase space at collisions of the moving particle with the replicated scatterer, where the angle α is used on the x-axis and $\sin\beta$ on the y-axis. The first plot in the upper 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.

H-function[2].

$$H(t) = \sum_i f_i(t) \ln f_i(t) \tag{2}$$

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_{KS} (which turns out to be the sum of all positive Lyapunov exponents):

$$N_t \sim \exp(h_{\text{KS}} t). \tag{3}$$

This leads to an H-function which decays linearly with time [29], starting from its initial value zero. The slope is given by h_{KS}. Obviously, the linear decay comes to an end when all available boxes are filled and $H(t)$ becomes constant. It is

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[2] 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]

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 Equ. (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 μ-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 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 Sec. 7. However, deterministic thermostats are often unable to equilibrate the dynamics of strong harmonic degrees of freedom [36, 37]. Particular techniques such as chains of coupled thermostats have been developed to overcome this problem [37, 38]. 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 by 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 than 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 Ref. [43] for an interesting account of the history of the fourth virial coeffcient, and Ref. [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-centerd-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"

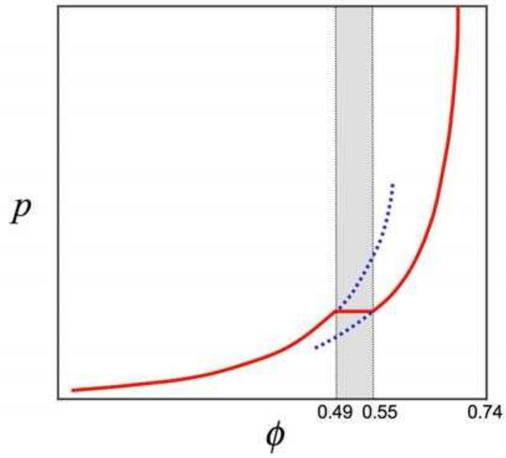

Figure 4. Pressure p as a function of the packing fraction ϕ for a system of hard spheres. The gray area indicates the coexistence region and the dotted lines are the metastable branches of the equations of state for the fluid and the solid phases.

held 1957 at the Stevens Instiute 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 even [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 $\phi = 0.49 - 0.55$ (the packing fraction ϕ 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 $\phi = \pi/18 \approx 0.74$ 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 Fig. 4), which indicates that the hard sphere freezing transition is indeed of first order. Recent experimental and computational studies have focused on the related intriguing question, if 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

$$F = U - TS \tag{4}$$

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,

$$S = k \log W, \tag{5}$$

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 Equ. (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 disorderd 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 ρ 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 $S(E) = -k_{\rm B} \ln \rho(E)$. 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 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 result 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 $10^{-3}k_\mathrm{B}$ 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.[3] 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

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[3] However, the transport coefficients depend on the wave vector in this case.

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 currently 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, such that colloidal systems are a fascinating new probing ground for statistical mechanical theories.

6 Fluctuation theorems and the Second Law

"The impossibility of an incompensated 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 systen 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 along which the entropy decreases must also exist. 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 dissipated work, 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 λ 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. Different values of λ correspond to different macroscopic states which may differ in free energy:

$$\Delta F = F_B - F_A = -k_{\mathrm{B}} T \ln \frac{\int dx \, e^{-\beta H(x,\lambda_B)}}{\int dx \, e^{-\beta H(x,\lambda_A)}}. \tag{6}$$

Now, if one switches the external parameter from an initial value λ_A to a final value λ_B in a finite time τ 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 λ,

$$\langle W \rangle \geq \Delta F. \tag{7}$$

The angular brackets denote an average over many realizations of the switchinng 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:

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta F). \tag{8}$$

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 can exceed the equilibrium free energy difference by far. Nevetheless, 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

$$\frac{P_R(-W)}{P_F(W)} = \exp[-\beta(W - \Delta F)]. \tag{9}$$

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-equilbrium processes at small length and time scales.

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 Woronow-

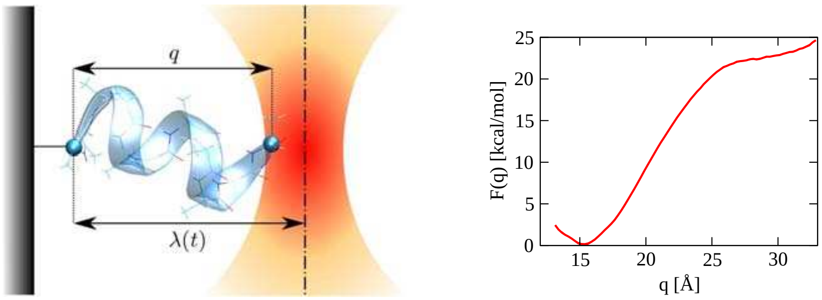

Figure 5. Modern micromanipulation equipment permits to exert well defined forces on single molecules and probe the free energetics of selected degrees of freedom. On the left-hand side a decaalanine molecule is stretched by a laser trap translated at constant speed (graphics by Harald Oberhofer, University 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].

icz 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 perpetuum mobile 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 does 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 partice, 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 Sec. 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 Fig. 6). On average, it experiences a 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 Fig. 6 for

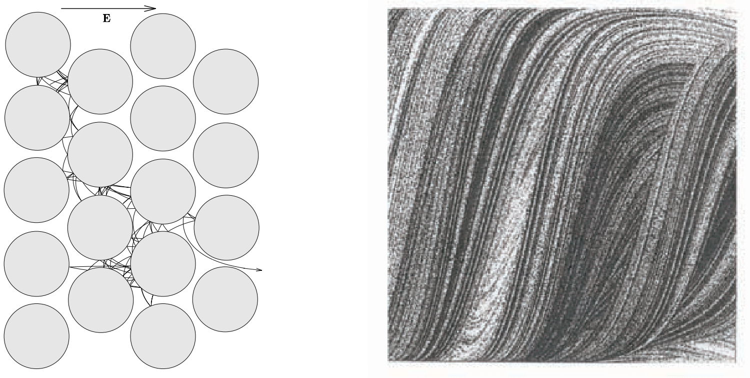

Figure 6. *Left panel:* Geometry and short trajectory of a periodic driven Lorentz gas. In addition to the elastic reflections, a constant force E and a Gauss thermostat acts on the wandering point particle. *Right panel:* Section of the phase-space probability in the stationary nonequilibrium state. The same coordinates as in Fig. 3 are used.

this case. Whereas in the absence of the perturbation the points are uniformly distributed as in the bottom-right panel of Fig. 3, the nonequilibrium stationary state of Fig. 6 is characterized by a multifractal phase-space distribution f, which is singular in every point. The following important chain of relations holds [97]:

$$\left\langle \frac{d \ln \delta V}{dt} \right\rangle = - \left\langle \frac{d \ln f}{dt} \right\rangle = - \frac{\dot{S}_{\mathrm{irr}}}{k_B} = \sum_{l=1}^{D} \lambda_l = -\langle \zeta \rangle < 0 \tag{10}$$

The first two equalities state that any infinitesimally-small phase volume δV, comoving with the phase flow, shrinks on average and leads to an attractor and a multifractal probability distribution f in phase space as shown in Fig. 6. Furthermore, the rate of irreversible entropy production, $\dot{S}_{\mathrm{irr}}$, 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. 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 irreversibilty 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 Eq. (10) and the conclusions drawn from them are not particular to this specific model, but - with very slight generalizations - apply to all stationary nonequiliibrium 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 μ-space. In the absence of external forces, the Boltzmann equation may be written in simplified form as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{f}{\mathbf{x}} = \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} . \tag{11}$$

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 μ-space element by the collisions. The Boltzmann equation is an approximate but nevertheless very complicated integro-differential equation. It can be analytically solved 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 Smoluchovski, 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 Sec. 6 in connection with recent fluctuation theorems, and in Sec. 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 informations 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 up to of 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 continuous 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 fundamental premise 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 of Bird [103], for instance, binary collisions between particles still occur, but the collisions are determined statistically rather then 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 Boltzmanns'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 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 aeordynamics 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 Fig. 7.

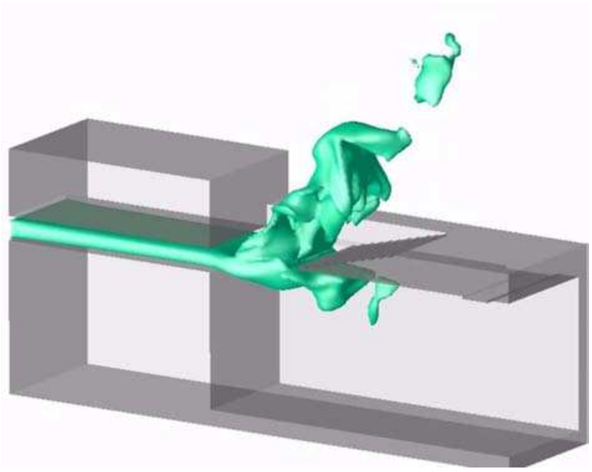

Figure 7. Complex air flow in a recorder as computed with the Lattice Boltzmann method. Shown in green is an iso-speed surface at 40% of the maximum jet speed (simulation and figure by Hemut Kühnelt, University of Vienna).

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 Bhatnar, 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.

Acknowledgments

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