Chapter 1

Introduction

1.1 The task of statistical physics

Statistical Physics is that part of physics which derives emergent properties of macroscopic matter from the atomic structure and the microscopic dynamics. Emergent properties of macroscopic matter mean here those properties (temperature, pressure, mean flows, dielectric and magnetic constants etc.) which are essentially determined by the interaction of many particles (atoms or molecules). Emergent means that these properties are typical for many-body systems and that they do not exist (in general) for microscopic systems. The key point of statistical physics is the introduction of probabilities into physics and connecting them with the fundamental physical quantity entropy. The first task of this new scientific discipline was to connect atomistics with thermodynamics.

atomistics → statistical mechanics → thermodynamics

More generally, the task is to construct the bridge between microphysics, i.e. properties and dynamics of atoms and molecules with macrophysics, i.e. thermodynamics, hydrodynamics, electrodynamics of media

microphysics → statistical physics → macrophysics

In this connection macrophysical properties designate those properties which are determined by the interaction of very many particles (atoms, molecules), in contrast to properties which are characteristic for one or a few particles. From the dynamical point of view a macrosystem is a many-body system which is determined by the basic equations of classical or quantum mechanics. Further basic elements of the theory should be the laws of interaction of the particles as, e.g. the Coulomb law, the symmetry principle and the boundary conditions characterizing the macroscopic embedding. From this point of view, the problem seems to be practically insolvable, not only for the impossibility to solve more than 10^{24} coupled usual or partial differential equations but also due to the incomplete knowledge about the initial and boundary conditions. This is the point, where new concepts are needed and it has to be shown that probabilities and/or density operators and entropies may be introduced in a natural way if the dynamics is unstable. The point of view taken in this textbook is mainly classical but the quantum-statistical analysis goes in many aspects in a quite analogous way. By using probabilities instead of trajectories, which is indeed a basic change of concepts (Prigogine and Stengers, 1984; Prigogine, 1989; Prigogine et al., 1991), we come to a dynamics of probabilities. In the classical case we obtain in this way the Liouville equation and in the quantum case the von Neumann equation:

microdynamics + probabilities → Liouville–von Neumann dynamics

This is a great step in the right direction since now macroscopic properties may be described as mean values and a macroscopic dynamics seems to be in reach. The remaining problem is however, that the Liouville–von Neumann equation are formally completely equivalent to the original dynamical equations, they are just a different expression of the same dynamics. In so far, the Liouville–von Neumann equation have still the property of reversibility of the microscopic dynamics. All conclusions based on these equations would not be in accord with the second law of thermodynamics. So, still a second step has to be made to arrive at an appropriate macroscopic dynamics. The basic idea is, that macroscopic processes allow and require a coarse-grained description. This point was worked out first by Gibbs and the Ehrenfest's. It means at first, that it makes no sense to describe a macroscopic process in all microscopic detail, since it completely impossible to observe all the details and to follow the trajectories of all particles. Instead of the fine description, a coarse-grained description must be introduced which still keeps the relevant macroscopic informations but neglects the irrelevant microscopic details. This idea is rather old but it was only recently understood, that the whole concept of coarse-graining is intimately connected with the instabilities of the microscopic trajectories (Nicolis et al., 1991). Finally we arrive at equations for the coarse-grained probabilities which are irreversible and yield an appropriate basis for the macroscopic physics. These equations are called kinetic equations or master equations. Our scheme may now be completed in the following way:

coarse-graining + dynamic instability → kinetic/master eqs.

The following chapters are aimed to work out this program, with some special attention to the concept of Brownian motion. But, before going in the details we would like to have another more historical oriented look at the development of the basic ideas and at the historical facts — admittedly with some bias to the development in Berlin, largely following earlier work (Rompe et al., 1987; Ebeling & Hoffmann, 1990, 1991).

1.2 On history of fundamentals of statistical thermodynamics

Thermodynamics as a branch of science was established in the 19th century by pioneers as Sadi Carnot (1796–1832), Robert Mayer (1814–1878), Hermann Helmholtz (1821–1894), William Thomson (1824–1907) and Rudolf Clausius (1822–1888). Evidently Mayer was the first who formulated the law of energy conservation. His paper "*Bemerkungen über die Kräfte der unbelebten Natur*" published 1842 in Liebig's Annalen is clearly expressing the equivalence of work and heat. Joule came to similar conclusions which were based on direct measurements concerning the conversion of work into heat. A great role in the foundation of thermodynamics played a community of physicists which worked in the middle of the 19th century in Berlin. Without doubt it was the genius of Hermann Helmholtz who determined the direction and the common style of research (Ebeling & Hoffmann, 1991). On July 23, 1847 he reported to the "*Berliner Physikalische Gesellschaft*", a new society founded by young physicists, about his research on the principle of conservation of energy. At 27 years of age Helmholtz was working as a military surgeon to a regiment of Hussars in Potsdam. He could follow his interest in physics only in his leisure time, since his family's financial situation did not allow him to enjoy full-time study. The experimental research which he carried out from the beginning of the 1840's in the laboratory of his adviser Professor Magnus was primarily devoted to the conversion of matter and heat in such biological processes as rotting, fermentation and muscular activity. Helmholtz's insight led him to infer a new law of nature from the complexities of his measurements on juices and extracts of meat and muscles. From experiments and brilliant generalization emerged the principle of conservation of energy or what is now called the first law of thermodynamics. Neither J.'R. Mayer nor J. P. Joule (not to speak of the other pioneers of the energy principle) recognized its fundamental and universal character as clearly as did Helmholtz, who must therefore be regarded as one of the discoverers of the principle, although his talk to the Berlin Physical Society was given later than the fundamental publications of Mayer and Joule. Both were unknown to Helmholtz at the time. Helmholtz had to fight hard for the recognition of his result — Professor Poggendorf, the influential editor of the "*Annalen der Physik und Chemie*", had no wish to publish what seemed to him rather speculative and philosophical. Magnus also regarded it with disfavor, but at least recommend that it be printed as a separate brochure, as was very quickly managed with the help of the influential mathematician C. G. Jacobi. The new law of nature quickly demonstrated its fruitfulness and universal applicability. For instance Kirchhoff's second law for electrical circuits is essentially a particular case of the energy principle. Nowadays these laws are among the most frequently applied laws in the fields of electrical engineering and electronics. The discovery of the fundamental law of circuits was done early in Kirchhoff's life in Königsberg and Berlin.

Rudolf Clausius (1822–1888) also played an essential role in the history of the law of conservation of energy and its further elaboration (Ebeling & Orphal, 1990). After studying in Berlin, he taught for some years at the Friedrich-Werdersches Gymnasium in Berlin and was a member of the seminar of Professor Magnus at the Berlin University. His report on Helmholtz's fundamental work, given to Magnus' colloquium, was the beginning of a deep involvement with thermodynamical problems. Building on the work of Helmholtz and Carnot he had developed, and published 1850 in Poggendorff's Annalen his formulation of the second law of thermodynamics. Clausius was fully aware of the impact of his discovery. The title of his paper explicitly mentions "*laws*". His formulation of the second law, the first of several, that heat cannot pass spontaneously from a cooler to a hotter body, expresses its essence already. Unlike Carnot, and following Joule, Clausius interpreted the passage of heat as the transformation of different kinds of energy, in which the total energy is conserved. To generate work, heat must be transferred from a reservoir at a high temperature to one at a lower temperature, and Clausius here introduced the concept of an ideal cycle of a reversible heat engine. In 1851 William Thomson (Lord Kelvin) formulated independently of Clausius another version of the second law. Thomson stated that it is impossible to create work by cooling down a thermal reservoir. The central idea in the papers of Clausius and Thomson was an exclusion principle: "*Not all processes which are possible according to the law of the conservation of energy can be realized in nature. In other words, the second law of thermodynamics is a selection principle of nature*". Although it took some time before Clausius' and Thomson's work was fully acknowledged, it was fundamental not only for the further development of physics, but also for science in general. In later works Clausius arrived at more general formulations of the second law. The form valid today was reported by him at a meeting of the "*Züricher Naturforschende Versammlung*" in 1865. There for the first time, he introduced the quotient of the quantity of heat absorbed by a body and the temperature of the body $d'Q/T$ as the change of entropy. The idea to connect the new science with the atomistic ideas arose already in the fifties of the 19th century. August Karl Krönig (1822–1879), extended thermodynamics and started with statistical considerations. In this way Krönig must be considered a pioneer of statistical thermodynamics. In 1856, he published a paper in which he described a gas as system of elastic, chaotically moving balls. Krönig's model was inspired by Daniel Bernoulli's paper from 1738, where Bernoulli succeeded in deriving the equation of state of ideal gases from a billiard model. Krönig's early attempt to apply probability theory in connection with the laws of elastic collisions to the description of molecular motion, makes him one of the forerunners of the modern kinetic theory of gases. After the appearance of Krönigs paper, Clausius admitted, that he too had been thinking about related problems since the late 1840s. In a subsequent paper "*Über die Art der Bewegung, die wir Wärme nennen*", which appeared 1857 in Vol. 100 of the *Annalen der Physik*, Clausius published his ideas about the atomistic foundation of thermodynamics. In fact, his work from 1857 as well as a following paper published in 1858 are the first comprehensive survey of the kinetic theory of gases. As a result of his work Clausius developed new terms like the mean free path and cross section and introduced in 1865 the new fundamental quantity entropy. Further we mention the proof of the virial theorem for gases, which he discovered in 1870. Parallel to Clausius's work the statistical theory was developed in Great Britain by James Clerk Maxwell, who derived in 1860 in an article in Philosophical Magazine the probability distribution for the velocities of molecules in a gas. In 1866 Maxwell gave a new derivation of the velocity distribution based on a study of direct and reversed collisions and formulated a first version of a transport theory. In 1867 Maxwell considered first the statistical nature of the second law of thermodynamics and considered the connection between entropy and information. His "*Gedankenexperiment*" about a demon observing molecules we may consider as the first fundamental contribution to the development of an information theory. In 1878 Maxwell proposed the new term "*statistical mechanics*".

This was, in brief, the situation when Ludwig Boltzmann (1844–1906) began his studies at the University of Vienna in 1863, the year when Josef Stefan (1835–1893) was appointed at the chair of physics of this University. He was deeply influenced by Stefan, who was a brilliant experimentalist and also by Johann Loschmidt (1821–1895) who was an expert in the kinetic theory of gases. In 1865 Loschmidt was the first who succeeded in estimating the diameter of molecules; based on this result, Planck calculated later the number of molecules in 1 cm^3 of a gas $N = 6.025 \cdot 10^{23}\ \mathrm{mol}^{-1}$. Influenced by the work of Stefan and Loschmidt as well as by studies of the papers of Clausius and Maxwell, Boltzmann started to work on the kinetic theory of gases. In 1866, he found the energy distribution for gases. In 1869, at the age of 25, Boltzmann was appointed as professor of mathematical physics in Graz. In 1871 he formulated the ergodic hypothesis, which is absolutely fundamental for the modern version of statistical physics and for the connection to nonlinear dynamics. The fruitful work in Graz culminated in 1872 with the formulation of Boltzmann's famous kinetic equation. In the same year 1872 he derived the H-theorem, which established a connection between mechanics and thermodynamics. The year 1872, which was so central for his work, was for Boltzmann also a year of traveling. He visited Bunsen and Königsberger in Heidelberg as well as Helmholtz and Kirchhoff in Berlin. The visit of Boltzmann to Berlin, which was rather influential for his further work, gives us the opportunity to consider, what happened in the mean time in Berlin. In 1871, after professorships in anatomy and physiology at several German universities, Helmholtz returned to Berlin to succeed Magnus as director of the physical institute of the university. Then began a very productive period in the history of physical research in Berlin. During the next two decades Helmholtz's direction of physical research in Berlin made it world famous. No burning questions of contemporary physics remained untouched by Helmholtz or his fellow workers, but thermodynamical problems remained central. Just as in the 1840s the social need for powerful and efficient power engines gave strong impetus to the discovery of the two laws of thermodynamics, so Helmholtz's late thermodynamical research was socially determined. The chemical industry, especially the large-scale production of fertilizers and dyes grew enormously during the second part of the nineteenth century, and necessitated a thermodynamic description of chemical processes. During Helmholtz's second period in Berlin his work revolved around pure and applied problems of thermodynamics. Using the general laws for thermodynamical and galvanic processes he advanced the theory and opened new fields of practical application. He developed the concept of free energy and investigated the relationship between the heat of reaction and the electromotive force of a galvanic cell. The thermodynamics of electrical double layers at boundaries also proved important when it became a keystone of modern physical chemistry and biophysics, as well as semiconductor electronics. We may also note that thermometric and calorimetric investigations dominated the activities of the Physikalische-Technische Reichsanstalt during Helmholtz's presidency. The studies of the properties and applications of light at the Reichsanstalt stimulated the scientific exploration of the physical basis of light generation, and led to the development of a thermodynamical theory of heat radiation. Helmholtz's pupil and coworker Wilhelm Wien (1864–1928) was a leader in this field and in collaboration with the Reichsanstalt he did very precise measurements of the spectral distribution of radiation, this way giving a sound basis for a theoretical interpretation. The critical analysis of Wien's formula and attempts to derive it from the basic laws of electrodynamics and thermodynamics formed the starting point for Max Planck's quantum theory. In 1889 Max Planck (1858–1947) was called to succeed Kirchhoff at the Berlin Chair of Theoretical Physics where he became one of the most famous of theoretical physicists at his time, in particular a world authority in the field of thermodynamics. He was a pioneer in understanding the fundamental role of entropy and its connection with the probability of microscopic states. Later he improved Helmholtz's chemical thermodynamics and his theory of double layers, as well as developed theories of solutions, including electrolytes, of chemical equilibrium and of the coexistence of phases. Planck was especially interested in the foundations of statistical thermodynamics. In fact he was the first who wrote down explicitely the famous formula

$$S = k \log W \,. \tag{1.1}$$

An independent and even more general approach to statistical thermodynamics and the role of entropy was developed by the great American physicists Josiah Willard Gibbs (1839–1903). Gibbs developed the ensemble approach, the entropy functional and was the first to understood the role of the maximum entropy method. His monograph on the principles of statistical physics is still the "bible" of statistical physics.

On the first glance the new field of physics developed by Boltzmann and Gibbs, called "statistical mechanics", "statistical thermodynamics" or "statistical physics" was beautiful, attractive to young scientists and very perspective. However soon it became clear that the new field is not free of contradictions and mathematical difficulties. This was criticized e.g. by one of the greatest mathematicians of that time Henri Poincare (1854–1912). Planck was also worried about these problems and asked his talented student, the mathematician Ernst Zermelo, to think about the mathematical foundation of Boltzmann's theory. In fact Boltzmann's theory was based on the idea that the equilibrium properties of a macroscopic system are the are the averages of phase functions of the microscopic state taken over an infinite time. Strictly speaking, the computation of time averages would require complete solution of the mechanical equation of an N-particle system. In practice, there is little to do with this concept for $N \gg 1$. Boltzmann sought to get around these difficulties by the introduction of the so-called "ergodic hypothesis". The latter says that the trajectory of a large system crosses every point of the energy surface. Zermelo found a serious mathematical objection against Boltzmann's theory which was based on the theorem of Poincare about the "quasi-periodicity of mechanical systems" published in 1890 in the paper "*Sur le probleme de trois corps les equations de la dynamique*". In this fundamental work Poincare was able to prove under certain conditions that a mechanical system will come back to its initial state in a finite time, the so-called recurrence time. Zermelo showed in 1896 in a paper in the "*Annalen der Physik*" that Boltzmann's H-theorem and Poincares recurrence theorem were contradictory. In spite of this serious objection, in the following decades statistical mechanics was dominated completely by ergodic theory. A deep analysis of the problems hidden in ergodic theory was given by Paul and Tatjana Ehrenfest in a survey article published 1911 in "*Enzyklopädie der Mathematischen Wissenschaften*". Much later it was recognized that the clue for the solution of the basic problem of statistical mechanics was the concept of instability of trajectories developed also by Poincare in 1890 in Paris. Before we study this new direction of research, we explain first the development of some other directions of statistical thermodynamics.

Planck reinforced the development of statistical thermodynamics through invitations to other leading specialists, such as Jacobus Henricus van't Hoff (1852–1911) whom, supported by Nernst and others, he nominated for a professorship at the Academy in Berlin. There van't Hoff had no teaching duties and could choose his topics of research absolutely freely. As the creator of a fruitful new branch of molecular physics he made important contributions to the thermodynamics of solutions and solution-salt equilibria. Furthermore he showed by thermodynamic methods the dependence of chemical equilibrium on temperature and pressure and discovered the fundamental laws of chemical kinetics, which remain the basis for the calculation of chemical processes. Finally he gave the first correct interpretation of osmotic pressure and introduced chemical affinity as the driving force for chemical reactions.

These last researches persuaded the Stockholm Nobel committee to award van't Hoff the first Nobel prize in chemistry (1901). Another important contribution to thermodynamics is connected with the work of Walther Nernst (1864–1941) who accepted in 1905 a call on a chair at the Berlin university. Nernst was one of the founders of physical chemistry and his work on the thermodynamical foundations of electrochemistry cemented his reputation as a leading contemporary scientist. In 1905 he detected the "missing stone in thermodynamics", the third law of thermodynamics. Nernst's seminal idea arose from the critical analysis of experimental data on chemical and electrochemical reactions in the liquid phase at low temperatures, where there appeared good correspondence between the free energy and the internal energy — M. P. Bertholet had already hypothesized the identity of these quantities, and Nernst found by his analysis that the correspondence improved at lower temperatures. This led him to suggest that the difference between the internal energy and free energy vanishes asymptotically at the zero temperature. Some years later Planck gave Nernst's new principles the following general and widely known formulation: "*The entropy of all bodies which are in internal equilibrium vanishes at the zero point of temperature*". After postulating his new theorem Nernst and his collaborators took great pains to prove and develop further this new law of nature. The specific heat, being of special importance, was determined for several substances at low temperatures. This was a very difficult scientific problem which called for the construction of equipment and instruments from scratch.

At the same time (1905/06) that Nernst's group was working on the experimental verification of the heat theorem, Einstein and Smoluchowski worked out the theory of Brownian motion. The first theoretical work of Albert Einstein (1879–1955) was carried out during he was working at the Bern patent office. Einstein started his work on statistical physics in 1902/03 with two very interesting papers on "*The kinetic theory of thermal equilibrium and the second law of thermodynamics*", published in leading physical journal of that time, the "*Annalen der Physik*". Here independently of Gibbs, Einstein developed the basic ideas of ensemble theory and the statistics of interacting systems. In his dissertation, presented in 1905 to the Zürich University, he developed a first correct theoretical interpretation of Brownian motion. This work was published in volume 17 of the "*Annalen der Physik*". Einstein was at that time only 26 years old, he published in the same volume of the "Annalen", also two other fundamental papers devoted to the theory of relativity and the theory of the photo effect. The first experimental check of Einstein's relations was published already in 1906 by Svedberg in the "*Zeitschrift für Elektrochemie*". In the same year appeared the first paper of Marian von Smoluchowski (1872–1917) who worked at that time as a professor at the University of Lemberg (Lviv) and contributed many fundamental results to the theory of Brownian motion. Because of the fundamental importance of this direction of research to statistical physics and in connection with the upcoming anniversary of the papers of Einstein and Smoluchowski we will discuss more details on the history of the concept of Brownian motion in an extra section.

In 1907, Einstein proposed that quantum effects lead to the vanishing of the specific heat at zero temperature. His theory may be considered as the origin of quantum statistics. Einstein's work attracted the attention of Nernst and his collaborators and by 1910 they succeeded in confirming this prediction. In this way the third law of thermodynamics as well as the young and still controversial quantum theory found one of its first experimental verifications. Through these investigations Nernst became not only one of the earliest and most committed prophets of the quantum theory — he was the initiator of the first Solvay conference (1911) — but also a firm supporter of the young Einstein. In 1913, together with Planck, he was able to bring the "*new Copernicus*" into the exclusive circle of Berlin physicists and they could offer the unconventional genius excellent working and living conditions. As a "*paid genius*" in Berlin, Einstein could complete his general theory of relativity, and make further important contributions to thermodynamics and statistical physics. In 1924, he gave a correct explanation of gas degeneracy at low temperatures by means of a new quantum statistics, the so-called Bose–Einstein statistics. In addition to the Bose–Einstein condensation his ideas about the interaction between radiation and matter should be emphasized. In 1916 his discussion of spontaneous emission of light and induced emission and adsorption forms the theoretical basis of the nonlinear dynamics and stochastic theory of lasers. Concerning many other fundamental contributions to thermodynamics and statistical physics in the last century we must restrict ourselves to brief remarks. The German-Greek mathematician Constantin Caratheodory formulated thermodynamics on an axiomatic basis. His analysis of such fundamental concepts as temperature and entropy in terms of the mathematical theory of Pfaffian differential forms were not appreciated by most of his contemporaries, although Planck was an early supporter of what has become one of the important branches of modern thermodynamics.

Another important line of the development of thermodynamics is the foundation of irreversible thermodynamics. We mention only the early work of Thomson, Rayleigh, Duhem, Natanson, Jaumann and Lohr. The final formulation of the basic relations of irreversible thermodynamics we owe to the work of Onsager (1931), Eckart (1940), Meixner (1941), Casimir (1945), Prigogine (1947) and De Groot (1951). Irreversible thermodynamics is essentially a nonlinear science, which needs for its development the mathematics of nonlinear processes, the so-called nonlinear dynamics.

The great pioneers of nonlinear dynamics in the 19th century were Helmholtz, Rayleigh, Poincare and Lyapunov. John William Rayleigh (1842–1919) is the founder of the theory of nonlinear oscillations. Many applications in optics, acoustics, mechanics and hydrodynamics are connected with his name. Alexander M. Lyapunov was a Russian mathematician, who formulated in 1982 the mathematical conditions for the stability of motions. Henri Poincare (1854–1912) was a French mathematician, physicist and philosopher who studied in the 1890s problems of the mechanics of planets and arrived at a deep understanding of the stability of mechanical motion. His work "*Les methodes nouvelles de la mechanique celeste*" (Paris 1892/93) is a corner stone of the modern nonlinear dynamics. Important applications of the new concepts were given by the engineers Barkhausen and Duffing in Germany and van der Pol in Holland. Heinrich Barkhausen (1881–1956) studied physics and electrical engineering at the Technical University in Dresden, were he defended in 1907 the dissertation "*Das Problem der Schwingungserzeugung*" devoted to to problem of selfoscillations. He was the first who formulated in a correct way the necessary physical conditions for self-sustained oscillations. Later he found worldwide recognition for several technical applications as e.g. the creation of short electromagnetic waves. Georg Duffing worked at the Technical High School in Berlin-Charlottenburg. He worked mainly on forced oscillations; a special model, the Duffing oscillator was named after him. In 1918 he published the monograph "*Erzwungene Schwingungen bei veränderlicher Eigenfrequenz und ihre technische Bedeutung*". Reading this book, one can convince himself that Duffing had a deep knowledge about the sensitivity of initial conditions and chaotic oscillations. A new epoch in the nonlinear theory was opened when A.A. Andronov connected the theory of nonlinear oscillations with the early work of Poincare. In 1929 he published the paper "*Les cycles limites de Poincare et la theorie des oscillations autoentretenues*" in the *Comptes Rendus Acad. Sci. Paris.* The main center of the development of the foundations of the new theory theory evolved in the 1930s in Russia connected with the work of Mandelstam, Andronov, Witt and Chaikin as well as in the Ukraina were N. M. Krylov, N. N. Bogoliubov and Yu. A. Mitropolsky founded a school of nonlinear dynamics.

That there existed a close relation between statistical thermodynamics and nonlinear science was not clear in the 19th century when these important branches of science were born. Quite the opposite, Henri Poincare, the father of nonlinear science, was the strongest opponent of Ludwig Boltzmann, the founder of statistical thermodynamics. In recent times we have the pleasure to see that Poincare's work contains the keys for the foundation of Boltzmann's ergodic hypothesis. The development of this new science had important implications for statistical thermodynamics. We have mentioned already the new concept of instability of trajectories developed by Poincare in Paris in 1890. This concept was introduced into statistical thermodynamics by Fermi, Birkhoff, von Neumann, Hopf and Krylov. The first significant progress in ergodic theory was made through the investigations of G. Birkhoff and J. von Neumann in two subsequent contributions to the Proceedings of the national Academy of Science U.S. in 1931/32. The Hungarian Johann von Neumann (1903–1957) came in the 1920s to Berlin attracted by the sphere of action of Planck and Einstein in physics and von Mises in mathematics. Von Neumann, who is one of the most influential thinkers of the 20th century made also important contributions to the statistical and quantum-theoretical foundations of thermodynamics. Von Neumann belonged to the group of "surprisingly intelligent Hungarians" (D. Gabor, L. Szilard, E. Wigner), who studied and worked in Berlin around this time. The important investigations of von Neumann on the connection between microscopic and macroscopic physics were summarized in his fundamental book "*Mathematische Grundlagen der Quantenmechanik*" (published in 1932). It is here that he presented the well known von Neumann equation and other ideas which have since formed the basis of quantum statistical thermodynamics. Von Neumann formulated also a general quantum-statistical theory of the measurement process, including the interaction between observer, measuring apparatus an the object of observation. This brings us back to Maxwell and in this way to another line of the historical development.

Information-theoretical considerations in statistical physics start with Maxwell's speculations about a demon observing the molecules in a gas. Maxwell was interested in the flow of information between the observer, the measuring apparatus and the gas. In fact this was the first investigation about the relation between observer and object, information and entropy. This line of investigation was continued by Leo Szilard, prominent assistant and lecturer at the University of Berlin and a personal friend of von Neumann. His thesis (1927) "*Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen*" investigated the connection between entropy and information. This now classic work is probably the first comprehensive thermodynamical approach to a theory of information processes and, as the work of von Neumann, deals with thermodynamical aspects of the measuring process. The first consequent approach to connect the foundations of statistical physics with information theory is due to Jaynes (Jaynes, 1957; 1985). Jaynes method was further developed and applied to nonequilibrium situations by Zubarev (Subarev, 1976; Zubarev et al., 1996, 1997)). The information-theoretical method is of phenomenological character and connected with the maximum entropy approach.

We have to mention also of the important contribution of Erwin Schrödinger to the foundation of statistical and biological thermodynamics. In 1927, Schrödinger succeeded Planck in the chair of theoretical physics. In the fall of 1933 he resigned from this post and after some years of travelling (England, Belgium, Austria) in 1939 he found his final refuge in Dublin. Here in 1944 he published the two little but very influential books "*Statistical Thermodynamics*" and "*What is Life?*", which considerably influenced the development of science and especially statistical thermodynamics and its applications to life sciences. The merit of the first comprehensive representation of the ideas of statistical thermodynamics in the framework of the ensemble theory belongs indisputably to Richard C. Tolman (1881–1948), who wrote the "*bible*" of modern statistical physics, the book "*The Principles of Statistical Mechanics*" (Oxford 1938). Another fundamental book which summarized the development of nonlinear mechanics was written at nearly the same time by the Russian scientists Andronov, Witt and Chaikin. The history of this book is a tragedy. After the book was in print, one of the authors, Witt, was arrested in Moscow for political reasons. He was placed in prison, where he eventually died. The first edition of the book appeared in 1941 under the Russian title "*Nelineinye Kolebaniya*" (i.e. "*Nonlinear Oscillations*") and the two named authors were only Andronov and Chaikin. Only the first German translation which appeared in 1959 corrected this crime (Andronov, Witt, Chaikin, 1959). The comprehensive books of Tolman at one hand and Andronov, Witt and Chaikin on the other stand at the end of the first century of development of our science. There is no room to discuss here the "explosion" of work after these two pioneering books, so we must restrict ourselves to occasional remarks during the text of the next chapters. Let us mention however that the first book on the connection between statistical physics and nonlinear science was published in 1950 by the Russian scientist N. M. Krylov. The title of his fundamental monograph was "*Works on the Foundation of Statistical Physics*".

1.3 On history of the concept of Brownian motion

Having the aim to derive macroscopic properties we have to look first at microscopic dynamics. As observed first by Ingenhousz and Brown, the microscopic motion of particles is essentially erratic. These observations led to the concept of Brownian motion which is basic to Statistical Physics. Moreover, the discussion of Brownian motion introduced quite new concepts of microscopic description, pertinent to stochastic approaches. The description put forward by Einstein in 1905/1906, Smoluchowski in 1906 and Langevin in 1908 is so much different from the one of Boltzmann: it dispenses from the description of the system's evolution in phase space and relies on probabilistic concepts. Marc Kac put is as follows: "*. . . while directed towards the same goal how different the Smoluchowski approach is from Boltzmann's. There is no dynamics, no phase space, no Liouville theorem — in short none of the usual underpinnings of Statistical Mechanics. Smoluchowski may not have been aware of it but he begun writing à new chapter of Statistical physics which in our time goes by the name of Stochastic processes*" (Fulinski, 1998). The synthesis of the approaches leading to the understanding of how the properties of stochastic motions are connected to deterministic dynamics of the system and its heat bath were understood much later in works by Mark Kac, Robert Zwanzig and others. A big part of this book is devoted to Brownian motion. For this reason and also having in mind the anniversary of the fundamentals of stochastic theory to be noticed in the years 2005–2008, we will discuss now the history of this important concept in some more detail.

The perpetual erratic motion of small particles immersed in a fluid was first observed as early as in 1785 by a Dutch physician Jan Ingenhousz; however, the phenomenon stayed unknown to the non-Dutch speaking community until it was rediscovered and studied in some detail by the Scottish botanist Robert Brown in

1827. Working on mechanisms of fertilization in plants, he turned his attention to the structure of pollen and concentrated at their microscopical characterization. Having observed the unceasing motion of the pollen in water he thought at first that the movement must be due to the living nature of the particles under observation. However, being a cautious scientist, he repeated his experiments with pollen kept in alcohol for several months (presumably dead) and with non-organic particles, which all showed similar behavior. (See one of the the Brown's original reports "*Additional Remarks on Active Molecules*" (Brown, 1829) and the discussion given by Brian J. Ford (1992).

The qualitative explanation of the Brownian motion as a kinetic phenomenon was put forward by several authors. In 1877 Desaulx wrote: "*In my way of thinking the phenomenon is a result of thermal molecular motion in the liquid environment* (*of the particles*)." In 1889 G. Gouy gave an account of detailed qualitative studies of the phenomenon (Gouy, 1889). He found that the Brownian motion is really a phenomenon which is not due to to random external influences (vibration, electric or magnetic fields) and that the magnitude of the motion depends essentially only on two factors: on the particles' size and on the temperature. In 1900 F. M. Exner undertook the first quantitative studies, measuring how the motion depends on these two parameters.

The ingenious microscopic derivation of the diffusion equation by Albert Einstein (which contained, in a nutshell, several different approaches) and the discussion by Paul Langevin put forward the two different approaches, one based on the discussion of the deterministic equations for the probability densities, another one based on the discussion of single, stochastic realizations of the process. These approaches, refined both from physical and from the mathematically point of view build now the main instrument of description of both equilibrium and nonequilibrium processes on a mesoscopic scale. Albert Einstein's first theoretical work was was carried out during he was working at the Bern patent office. Einstein started his work on statistical physics in 1902–1903 with two very interesting papers published in his favorite journal the "Annalen der Physik". Here independently of Gibbs, Einstein developed the basic ideas of ensemble theory and the statistics of interacting systems. In 1905 he presented a dissertation to the Zürich University which contains a theory of Brownian motion. Einsteins work which appeared in 1906 in the Annalen der Physik is the true origin of stochastic theory in physics, one of the corner stones of modern statistical thermodynamics.

In fact Einstein work was a theoretical discussion of one of possible consequences of the molecular-kinetic theory of heat: "*Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen*". In this work Einstein discusses that the kinetic theory of heat predicts the unceasing motion of small suspended particles (Einstein, 1905). He was not sure that the phenomenon discussed is exactly the Brownian motion, but considered this as a reasonable hypothesis. After publication of the work, Siedentopf and

Gouy pointed out that the effect he discussed was really the Brownian motion, since not only the qualitative properties, but also the predicted orders of magnitude of the effect were correct, as discussed in the Einstein's second work (Einstein, 1906).

Let us briefly discuss now Einstein's approach. More technical details will be explained in Chapter 7. Einstein, in his analysis of the situation has connected the motion of suspended particles with diffusion and showed that this diffusive behavior follows from the three postulates. First, the particles considered are the assumed not to interact with each other: their trajectories are independent. Second, one assumes that the motion of the particles lacks the long-time memory: one can chose such a time interval τ, that the displacements of the particle during two subsequent intervals are independent. Third, the distribution of the particle's displacements s during the subsequent time intervals $\phi(s)$ is symmetric and possesses at least two moments. The displacement of the particle can thus be considered as a result of many small, independent, equally distributed steps. The further line of his reasoning is very close to what is called now a Kramers–Moyal expansion. This line of reasoning was also adopted by Smoluchowski, who however, assumed a more radical approach based on combinatorics. Next step was made by Adriaan Daniel Fokker (1887–1972) in his dissertation. However, the short publication (Fokker, 1914) did not contain the details of his derivation and concentrated essentially only on the treatment of the stationary case. A more general approch was developed by Max Planck, who formulated a general transport equation for diffusive motion, now known as the Fokker–Planck equation (Planck, 1918).

Essential contributions, independently of Einstein, to this line of research we owe to the work of the great Polish physicist Marian von Smoluchowski (1872–1917) published in subsequent contributions to the Annalen der Physik beginning with 1906. In the first published work (Smoluchowski, 1906) he claimed that his method, consequently based on probabilistic ideas, is "*more direct, simpler and thus more convincing than one of Einstein*". The theory of Brownian motion stayed the main topic of the scientific activity of M. Smoluchowski until his sudden death in 1917. One of his last published works "*Versuch einer mathematischen Theorie der Kogulationskinetik kolloidaler Lösungen*" published in 1917 (Smoluchowski, 1917) has put foundation to the theory of diffusion-controlled reactions, and this line of argumentation was pursued by Peter Debye, Hendrik Anthony Kramers, and many others, see Chapters 10–11.

The macroscopically measurable fluctuations gave new experimental possibilities and several famous experimentalists were fascinated by the behavior of mesoscopic particles (Perrin measured Loschmidt's number and determined Planck's constant, Millikan and Ehrenhaft made experiments to define the elementary charge, Houdijk and Zeeman observed the motion of platin wires). The French physicist Paul Langevin (1872–1946) has to be mentioned who added random forces to the dynamical laws initiating thereby a new mathematical fruitful field, that of stochastic differential equation. Further we mention the dissertations of two young scientists,

L. Ornstein and G. Uhlenbeck, presented in 1908 and 1927 respectively to the University of Leiden as well as their subsequent publications.

The formulation of the quantitative theory by Einstein and by Smoluchowski (1906) motivated new, quantitative experiments performed by J.-B. Perrin (starting from 1908), A. Westgren, E. Kappler and many others. Perrin's work was crowned by the Nobel prize in 1926. These works put the firm foundation to the modern understanding of both equilibrium and non-equilibrium phenomena.

We will say now a few words on the completely different alternative approach to Brownian motion which is based on the concept of the Langevin equation. In his article published in *Comptes Rendus* in 1908 Paul Langevin proposed another approach to description of Brownian motion, than the one of Einstein and Smoluchowski. This one was assumed to be "infinitely simpler" than the Einstein's one and seemed to be only based on the equipartition theorem (Langevin, 1908).

The fruitful idea of Langevin was that the motion of the Brownian particle in fluid is governed by the Newtonian dynamics under friction, which for a for a macroscopic spherical particle follows the Stokes law. However, this behavior, leading to the continuous decay of the particle's velocity, holds only on the average. In order to describe the erratic motion of the particle, resulting from random, uncompensated impacts of the molecules of surrounding fluid, one has to introduce an additional, fluctuating force ("noise"). Adding fluctuating noise to deterministic equation is now a starting point of many fruitful theoretical approaches; the mathematics of such approaches, however, had first to be clarified by works of Kiyosi Ito (born 1915) and of Ruslan Stratonovich (1930–1997).

So far we talked about standard Brownian motion. This is the passive stochastic motion of microscopic objects due to random collisions from the side of the surrounding medium. In recent times the concept of Brownian motion is actively developing. At first we mention the development of the theory of active Brownian motion which considers self-propelling particles (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000; Mikhailov and Cahlenbuhr, 2002; Schweitzer, 2003). This new theory and several applications will be explained in Chapter 12. A funny note about the difference between standard and active Brownian motion is on place. Microbiologists claim, they can visually distinguish the Brownian motion of the essentially passive particles from the motion of the self-propelling ones. The students are trained to see the difference. However, the differences in the motion pattern is not so evident, so that many well-trained and famous scientists described the essentially immobile bacteria as mobile ones: This mistake happened to the great Japanese microbiologist Kitasato with the pest bacterium, as well as to his pupil Shiga and to the American Flexner with two different types of dysentery bacteria: All these scientists described the essentially immobile bacteria as self-propelling (Winkle, 1999).

The interrelation between theory of stochastic processes and biological problems is older and deeper than it might seem. In 1905 Karl Pearson, engaged in biostatistical problems, wrote a short letter to the journal Nature (Pearson 1905): "*Can any of you readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution provide me with an original one? I should be extremely grateful for the aid in the matter. A man starts from the point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. Inquire the probability that after n stretches he is at a distance between r and $r + \delta r$ from his starting point O*". This was the birth of the term "random walk", of a discrete stochastic model which got to be one of the most successful and important models of the whole statistical physics. The asymptotic solution of the problem for large number of steps was immediately given by Rayleigh, who referred to his old publication on summation or random oscillations (Rayleigh, 1880). The whole nature of the random walk approaches (taking into account discrete events on lowest scales, either as jumps, or as a continuous, homogeneous motion interrupted by scattering events (in the sense of the Paul Drude's approach to metals), as well as mathematical approaches to the problem, look very much different from typical continuous approaches used in theoretical physics. The model, however, is more adequate than, say, the Langevin approach fully neglecting local dynamics, for the description of such processes as hopping conductivity in strongly disordered semiconductors, transport processes in hydrology, and many others, and leads to a powerful and beautiful mathematics of fractional diffusion and Fokker–Planck equations (see Hilfer, 2000, Sokolov et al., 2002, West, 2003). The corresponding results will be discussed in Chapter 11 of our book.

The first random walk model was, however, put forward five years before Einstein's and Smoluchowski's work in the doctoral thesis of Louis Bachelier (1870–1946), defended and published in Paris in 1900. The thesis worked out mathematically the idea that the stock market prices with their unceasing ups and downs are essentially sums of independent, bounded random changes (Bachelier, 1900). The report on this thesis written by H. Poincaré can be found in the work of Taqqu (2002). It is sometimes claimed that the thesis was written under the supervision of H. Poicaré; this statement doesn't seem to be true: Bachelier worked and studied at the same time, he took courses occasionally, and probably presented his theses as the "external" candidate. Poincare, who disliked probabilistic approaches, made a positive note that the author "does not exaggerate the range of his results, and I do not think that he is deceived by his formulas."

Bernard Bru puts the situation as follows: "It was a thesis on mathematical physics, but since it was not physics, it was about the Stock Exchange, it was not a recognized subject" (see Taqqu, 2002). Note that application of physical methods to analysis of economical systems is now a rather well established branch of statistical physics; and a word "Econophysics" was coined to describe this field, see Stanley, 2003. Thus, the issues 1 and 2 of Volume 324 of journal **Physica A: Statistical Mechanics and its Applications** published the proceedings of the International

Econophysics Conference. We, however, will not discuss econophysical applications in this book, and we shall confine ourselves to classical application fields pertinent to physics, and partly to chemistry and biology.

The results put forward by Bachelier were of highest importance, and (partly used, partly rediscovered by later workers) lead to a flash of interest to stochastic processes and corresponding probabilistic approaches. The mathematical approaches (culminating in work by Norbert Wiener, Paul Lévy and Andrei Nikolaevich Kolmogorov) in the direction of formulating and refining stochastic approaches lead to a large body of knowledge giving a solid basis for modern applications in statistical physics. The purely mathematical discussion of limit theorems for the sums of independent, identically distributed random variables, connected mostly with the name of Lévy, lead to the results pertinent to the distributions lacking the dispersion, or even the mean. Such distributions are not as unphysical as they may seem, some of the modern applications in physics are discussed in the book of Shlesinger (1996).