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Material selected from the book:

Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems

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Chapter 1

Introduction
(selected topics)

1.1 The task of statistical physics

Statistical Physics is that part of physics which derives emergent properties of macroscopic matter from the atomic properties and 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.

atomistics $\rightarrow$ statistical mechanics
$\rightarrow$ thermodynamics and transport

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 $\rightarrow$ statistical physics
$\rightarrow$ macrophysics

Mmacrophysical properties = 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.

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.

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.

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.

Using probabilities instead of trajectories
we come to a dynamics of probabilities.
In the classical case: Liouville equation
in the quantum case: von Neumann equation:

microdynamics + probabilities
→ Liouville - von Neumann dynamics

Macroscopic properties may be described as mean values
However: Liouville - von Neumann equation are formally completely equivalent to the original dynamical equations.
have still the property of reversibility of the microscopic dynamics.
Conclusions based on these equations would not be in accord with the second law of thermodynamics
So, a second step has to be made.
The basic idea is, that macroscopic processes allow and require a coarse-grained description (Gibbs and the Ehrenfest's).
1) 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. 2) a coarse - grained description keeps the relevant macroscopic informations but neglects the irrelevant microscopic details.
it was only recently understood, that the whole concept of coarse - graining is intimately connected with the instabilities of the microscopic trajectories 3) 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

19th century pioneers :
Sadi Carnot (1796-1832),
Robert Mayer (1814-1878),
Hermann Helmholtz (1821-1894),
William Thomson (1824-1907)
Rudolf Clausius (1822-1888).
Evidently Mayer was the first who formulated the law of energy conservation. His paper 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.
Physicists which worked in the middle of the 19th century in Berlin: The genius of **Hermann Helmholtz** determined the direction and the common style of research
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
bf 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. **1965 Clausius gave more general forms 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 developed the kinetic approach

In a 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 derived in 1860 the prob distribution for velocities of molecules in Philosophical Magazine (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"*.

Ludwig Boltzmann (1844-1906)

began his studies at the University of Vienna in 1863, 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. Boltzmanns kinetic theory of gases:

In 1866, he found the energy distribution for gases.

In 1871 he formulated the ergodic hypothesis ,

In 1872 formulation of Boltzmanns famous kinetic equation and the H-theorem.

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 explicitly the famous formula

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

The great american pioneer
Josiah Willard Gibbs (1839 - 1903):
developed the ensemble approach, the entropy functional and was the first to understood the role of the maximum entropy method.

The new field is not free of contradictions and mathematical difficulties: criticized e.g. by
Henri Poincare (1854 - 1912) followed by Zermelo: stated problems of mathematical foundation of Boltzmann's theory.
Probles with the "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 Boltzmanns 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 Boltzmanns 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 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.

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. **In 1924 Einstein 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.

Another important line of the development of thermodynamics is the foundation of **irreversible thermodynamics**.
We mention 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.

The information-theoretical approach to 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)) and by Stratonovich. The information-theoretical method is of phenomenological character and connected with the maximum entropy approach.

On history of the concept of Brownian motion

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 a new chapter of Statistical physics which in our time goes by the name of Stochastic processes"
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 our 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 prepared a separate material on the history of this important concept.

Problems:
What is the main difference (with respect to terminology and basic equations) between the standard approach to statistical mechanics (Boltzmann, Gibbs)
and the stochastic approach by Smoluchowski, Einstein, Fokker, Planck et al.?
(See the view of Marc Kac and have a look at some original papers as far as available!)

Chapter 2

Thermodynamic, Deterministic and Stochastic Levels of Description (Selected results)

2.1 Thermodynamic level

First Law:

There exists a fundamental extensive thermodynamic variable E. Energy can neither be created nor be destroyed. In can only be transferred or changed in form. Energy is conserved in isolated systems. The energy production inside the system is zero.

$$dE = d_e E + d_i E \qquad (2.1)$$

$$d_i E = 0 \qquad (2.2)$$

Any process is connected with a transfer $d_e E$ or with a transformation of energy. Energy transfer may have different forms as heat, work and chemical energy. The unit of energy is $1J = 1Nm$, corresponding to the work needed to move a body 1 meter against a force of 1 Newton. An infinitesimal heat transfer we denote by $d'Q$ and the infinitesimal work transfer by $d'A$. If there is no other form of transfer, i.e. the system is closed, we find for the energy change (balance of energy):

$$dE = d_e E = d'Q + d'A \qquad (2.3)$$

In other words, the infinitesimal change of energy of a system equals the sum of of the infinitesimal transfers of heat and work. This is a mathematical expression of the principle given above: A change of energy must be due to a transfer, since creation or destruction of energy is excluded. If the system is **open**, i.e. the exchange of matter in the amount dN_i per sort i is admitted, we assume

$$dE = d'Q + d'A + \sum_i \mu_i dN_i \qquad (2.4)$$

Here the so-called chemical potential μ_i denotes the amount of energy transported by a transfer of a unit of the particles of the chemical sort i . Here μ_i has the dimension of energy per particle or per mole. The infinitesimal work has in the simplest case the form

$$d'A = -pdV \tag{2.5}$$

In the case that there are also other forms of work we find more contributions having all a bilinear form

$$d'A = \sum_k l_k dL_k \tag{2.6}$$

where l_k is intensive and L_k is extensive and in particular we have $l_1 = -p$ and $L_1 = V$. Strictly speaking this expression for the infinitesimal work is valid only for reversible forms of work. Later we shall come back to the irreversible case. In this way the balance equation for the energy changes (2.6) assumes the form

$$dE = d'Q + \sum_k l_k dL_k + \sum_i \mu_i dN_i \tag{2.7}$$

In this equation there remains only one quantity which is not of the bilinear structure, namely the infinitesimal heat exchange $d'Q$. The hypothesis, that bilinearity holds also for the infinitesimal heat, leads us to the next fundamental quantity, the entropy. We shall assume that $d'Q$ may be written as the product of an intensive quantity and an extensive quantity. The only intensive quantity which is related to the heat is T and the conjugated extensive quantity will be denoted by S. In this way we introduce entropy als the extensive quantity which is conjugated to the temperature:

$$d'Q = TdS \tag{2.8}$$

This equation may be interpreted also in a different way by writing following Clausius

$$dS = \frac{d'Q}{T} \tag{2.9}$$

The differential of the state variable entropy is given by the infinitesimal heat $d'Q$ divided by the temperature T. In more mathematical therms, the temperature T is an integrating factor of the infinitesimal heat.

The variable entropy was introduced in 1865 by Clausius. The unit of entropy is $1J/K$. One can easily show that this quantity is not conserved. Let as consider for example two bodies of different temperatures T_1 and T_2 being in contact. Empirically we know that there will be a heat flow from the hotter body 1 to the cooler one denoted by 2 . We find

$$d'Q_1 = T_1 dS_1 = d'Q = T_2 dS_2 \tag{2.10}$$

Due to our assumption $T_1 > T_2$ we get $dS_1 < dS_2$, i.e. heat flow down a gradient of temperature produces entropy. The opposite flow against a gradient of temperature is never observed.

A generalization of this observations leads us to the

Second Law of thermodynamics:

Thermodynamic systems possess the extensive state variable entropy. Entropy can be created but never be destroyed. The change of entropy in reversible processes is given by the exchanged heat divided by the temperature. During irreversible processes entropy is produced in the interior of the system. In isolated systems entropy can never decrease.

Let us come back now to our relation (2.7) which reads after introducing the entropy by eq. (2.8)

$$dE = TdS + \sum_k l_k dL_k + \sum_i \mu_i dN_i \tag{2.11}$$

This equation is called *Gibbs fundamental relation*. Since the Gibbs relation contains only state variables it may be extended (with some restrictions) also to irreversible processes. In the form (2.13) it may be interpreted as a relation between the differentials dE, dS, dL_k and dN_i . Due to the Gibbs relation one of those quantities is a dependent variable. In other words we may write e.g.

$$E = E(S, L_k, N_i)$$

or

$$S = S(E, L_k, N_i).$$

In order to avoid a misunderstanding, we state explicitely: *"The Gibbs fundamental relation was obtained from a balance, but primarily it is relation between the extensive variables of a system"*. Since this point is rather important, let as repeat it again: Eq.(2.6) expresses a balance between the energy change in the interior dE (the l.h.s of the eq.) and the transfer of energy forms through the border (the r.h.s.). On the other hand eq. (2.13) expresses the dependence between state variables, i.e. a completely different physical aspect. For irreversible processes the Gibbs relation (2.13) remains unchanged, at least in cases where the energy can still be expressed by the variables S, L_k, N_i . On the other hand the balance (2.6) has to be modified for irreversible processes. This is due to the fact that there exists a transfer of energy which passes the border of the system as work and changes inside the system into heat. Examples are Ohms heat and the heat due to friction. In the following we shall denote these terms by $d'A_{dis}$. Taking into account those contributions, the balance assumes the form

$$dE = d'Q + \sum_k l_k dL_k + d'A_{dis} + \sum_i \mu_i dN_i \tag{2.12}$$

For later applications we formulate now the first and the second law in a form due to Prigogine (1947). The balance of an arbitrary extensive variable X may be always written in the form

$$dX = d_e X + d_i X \tag{2.13}$$

where the index "e" denotes the exchange with the surrounding and the index "i" the internal change. Then the balances for the energy and the entropy read

$$dE = d_eE + d_iE, \qquad (2.14)$$
$$dS = d_eS + d_iS \qquad (2.15)$$

Further the first and the second laws respectively assume the mathematical forms

$$dE = d_eE; \qquad d_iE = 0$$

$$d_eE = d'Q + d'A + \sum_i \mu_i d_e N_i$$

$$d_eS = \frac{d'Q}{T}$$

$$dS \geq d_eS; \qquad d_iS \geq 0. \qquad (2.16)$$

This writing is especially useful for our further considerations. We mention that the relation for d_eS is to be considered as a definition of exchanged heat. The investigations of De Groot, Mazur and Haase have shown that for open systems other definitions of heat may be more useful. As to be seen so far, the "most natural" definition of heat exchange in open systems is

$$d_eS = \frac{d^*Q}{T} + \sum_i s_i d_e N_i \qquad (2.17)$$

The new quantity d^*Q is called the *reduced heat*; while $d'Q$ is called here the *entropic heat*. Further s_i is the specific entropy carried by the particles of kind i . The idea which led to the definition (2.18) is, that the entropy contribution which is due to a simple transfer of molecules should not be considered as a proper heat. Another advantage of the reduced heat is, that it possesses several useful invariance properties (Haase, 1963; Keller, 1977). The first and the second laws of thermodynamics formulated above are a summary of several hundred years of physical research. They constitute the most general rules of prohibition in physics.

2.2   Lyapunov Functions: Entropy and Thermodynamic Potentials

As stated already by Planck, the most characteristic property of irreversible processes is the existence of so-called Lyapounov functions. This type of function was defined first by the russian mathematician Lyapunov more than a century ago. A Lyapunov function is a non-negative function with the following properties

$$L(t) \geq 0, \qquad \frac{dL(t)}{dt} \leq 0. \qquad (2.18)$$

As a consequence of these two relations, Lyapunov functions are per definition never increasing in time.

Our problem is now to find a Lyapunov function for an arbitrary macroscopic system. Let us assume that the system is initially ($t = 0$) in a nonequilibrium state, and that we are able to isolate the given system for $t > 0$ from the surrounding. From the the definition of equilibrium follows that, after isolation, changes will occur. Under conditions of isolation the energy E will remain fixed, within the natural uncertainties, but the entropy will monotoneously increase due to the second law. Irreversible processes connected with a positive entropy production $P \geq 0$ will drive the system finally to an equilibrium state located at the same energy surface. In thermodynamic equilibrium, the entropy assumes the maximal value

$$S_{eq}(E, X)$$

which is a function of the energy and certain other extensive variables. The total production of entropy during the process of equilibrization of the isolated system may be obtained by integration of the entropy production over time.

$$\Delta S(t) = \int_0^t P(t)dt \tag{2.19}$$

Due to the condition of isolation, there is no exchange of entropy during the whole process. Due to the non-negativity of the entropy production

$$\frac{d_i S}{dt} = P(t) \geq 0 \tag{2.20}$$

the total production of entropy $\Delta S(t)$ is a monotonously non-decreasing function of time. The concrete value of $\Delta S(t)$ depends on the path γ from the initial to the final state and on the rate of the transition processes. However the maximal value of this quantity $\Delta S(\infty)$ should observe some special conditions.

Just for the case that the transition occurs without any entropy exchange, this quantity should be identical with the total entropy difference between the initial state and the equilibrium state at time $t \to \infty$

$$\delta S = S_{eq}(E, X) - S(E, t = 0) \tag{2.21}$$

This is the so-called entropy lowering which is simply the difference between the two entropy values. By changing parameter values infinitely slow along some path γ we may find a reversible transition and calculate the entropy change in a standard way e.g. by using the Gibbs fundamental relation (2.13). An important property of the quantity δS is, that it is independent on the path γ from the initial state to the equilibrium state. On the other hand the entropy change on an irreversible path may depend on details of the microscopic trajectory. In average over many realizations (measurements) should hold

$$\langle \Delta S(\infty) \rangle = \langle \int_0^\infty P(t)dt \rangle = \delta S \tag{2.22}$$

This equality follows from the fact that S is a state function, its value should be independent on the path on which the state has been reached. Assuming for a moment that the equality (2.24) is violated we could construct a cyclic process which contradicts the second law. The macroscopic quantity

$$\Delta S = \langle \Delta S(\infty) \rangle \tag{2.23}$$

may be estimated by averaging the entropy production for many realizations of the irreversible approach from the initial state to equilibrium under conditions of strict isolation from the outside world. The result

$$\Delta S = \delta S \tag{2.24}$$

is surprising: It says that we can extract equlibrium information δS from nonequilibrium (finite-time) measurements of entropy production. We will come back to this point in the next section. Here let us proceed on the way of deriving Lyapunov functions.

By using the relations given above we find for macroscopic systems the following Lyapunov function

$$L(t) = \Delta S - \Delta S(t) \tag{2.25}$$

which yields for isolated systems (Klimontovich, 1992, 1995)

$$L(t) = S_{eq} - S(t)$$

Due to

$$\frac{dL(t)}{dt} = -P(t) \leq 0 \tag{2.26}$$

and

$$\Delta S \geq \Delta S(t) \tag{2.27}$$

the function $L(t)$ has indeed the necessary properties (2.18) of a Lyapunov function.

Let us consider now a system which is in contact with a heat bath of temperature T. Following Helmholtz we define the characteristic function

$$F = E - TS \tag{2.28}$$

which is called the *free energy*. According to Gibbs' fundamental relation the differential of F is given by

$$dF = dE - TdS - SdT$$

$$= \sum_k l_k dL_k + \sum_i \mu_i dN_i - SdT \tag{2.29}$$

In this way we see that the proper variables for the free energy are the temperature and the extensive variables L_k (note $L_1 = V$) and N_i with $(i = 1, ...s)$. In other words we have

$$F = F(T, L_k, N_i)$$

The total differential (2.31) may also be considered as a balance relation for the free energy change for a quasistatic transition between two neighboring states. Let us now consider the transition under more general situations admitting also dissipative elements. Then we find

$$dF = dE - SdT - TdS =$$

$$d'A - d'Q - SdT - Td_eS - Td_iS.$$

$$dF = d'A - SdT - Td_iS \tag{2.30}$$

At conditions where the temperature is fixed and where the exchange of work is excluded we get

$$dF = -Td_iS \le 0; \qquad \frac{dF}{dt} = -TP \le 0 \tag{2.31}$$

As a consequence from eq. (2.31), the free energy is a nonincreasing function for systems contained in a heat bath which excludes exchange of work. At these conditions the free energy assumes its minimum F at the thermal equilibrium. Consequently the Lyapounov function of the system is given by

$$L(t) = F(t) - F_{eq} \tag{2.32}$$

which possesses the necessary Lyapunov properties (2.18). Another important situation is a surrounding with given temperature T and pressure p. The characteristic function is then the free enthalpy (Gibbs potential)

$$G = E + pV - TS \tag{2.33}$$

with the total differential

$$dG = dE - pdV - Vdp - SdT - TdS \tag{2.34}$$

and the balance relation

$$dG = d'A - d'Q - Vdp - pdV - SdT - Td_eS - Td_iS$$

$$= Vdp - SdT - Td_iS. \tag{2.35}$$

For given temperature and pressure we get

$$dG = -Td_iS \le 0$$

$$\frac{dG}{dt} = -TP \le 0 \tag{2.36}$$

Consequently the free enthalpy G is a non-increasing function for systems imbedded in an isobare and isothermal reservoir. In thermal equilibrium the minimum G_{eq} is assumed. Therefore

$$L(t) = G(t) - G_{eq} \tag{2.37}$$

is a Lyapunov function possessing the necessary properties (2.27-28). Let us consider now the most general situation, where our system is neither isolated nor in a reservoir with fixed conditions during its course to equilibrium. In the general case the Lyapounov function may be defined by

$$L(t) = S_{eq}(E(t=0), X) - S(E, t=0) - \int_0^t P(t')dt' \qquad (2.38)$$

This function has again the necessary properties of a Lyapunov function (2.27-28), i.e. it is non-negative and non-increasing. However it will tend to zero only under the condition of total isolation during the time evolution.

The definition of the entropy production is in general a non-trivial problem. In the special case however that the only irreversible process is a production of heat by destruction of mechanical work the definition of $P(t)$ is quite easy. Since then $P(t)$ is given as the quotient of heat production and temperature, a calculation of $L(t)$ requires only the knowledge of the total mechanical energy which is dissipated.

2.3   Energy, entropy, and work

Energy, entropy and work are the central categories of thermodynamics and statistical physics. The fundamental character of these phenomenological quantities requires our full attention. The entropy concept closes the gap between the phenomenological theory and the statistical physics. In spite of the central position of energy, entropy and work in physics, there exist many different definitions and interpretations (Zurek, 1990). Below we will be concerned with several these interpretations. We introduce mechanical energy, heat and work. Furtheron we talk about the Clausius entropy, the Boltzmann entropy, the Gibbs entropy, the Shannon entropy and Kolmogorov entropy. Extending the categories of energy and entropy to other sciences the confusion may even increase. In order to avoid any misinterpretation one has to be very careful when talking about these categories. However there should be no dought, that energy and entropy are central quantities. But due to their fundamentality a specific difficulty of philosophical character arises: It is extremely difficult or even impossible to avoid tautologies in their definition. In conclusion we may say that energy and entropy should be elements of an axiomatics of science. As we memntioned above, the difficulty in defining fundamental quantities was already discussed by Poincare with respect to energy. In his lectures on thermodynamics (1893) Poincare' says:

   "In every special instance it is clear what energy is and we can give at least a provisional definition of it; it is impossible however, to give a general definition of it. If one wants to express the (first) law in full generality,... , one sees it dissolve before one's eyes, so to speak leaving only the words: There is something, that remains constant (in isolated systems)."

   We may translate this sentence to the definition of entropy in the following way: *"In every special instance it is clear what entropy is and we can give at least a provisional definition of it; it is impossible however, to give a general definition of it. If one wants to express the second*

law in full generality, ... , one sees it dissolve before one's eyes, so to speak leaving only the words: There is something, that is non-decreasing in isolated systems".

In this way our definition of entropy is finally: Entropy is that fundamental and universal quantity characterizing a real dynamical system, that is non-decreasing in isolated systems. Energy and entropy are not independent, but are connected in a rather deep way. Our point of view is based on a valoric interpretation (Ebeling, 1993). This very clear interpretation will be taken as the basis for a reinterpretation of the various entropy concepts developed by Clausius, Boltzmann, Gibbs, Shannon and Kolmogorov. As the key points we consider the value of energy with respect to work. The discussion about this relation started already in the last century and is continuing till now. The valoric interpretation was given first by Clausius and was worked out by Helmholtz and Ostwald. But then, due to a strong opposition from the side of Kirchhoff, Hertz, Planck and others, it was nearly forgotten except by a few authors (Schöpf, 1984; Ebeling and Volkenstein, 1990). As a matter of fact however, the valoric interpretation of the entropy, was for Clausius itself the key point for the introduction of this new concept in 1864-65. What many physicists do not know is that the entropy concept taught in universities as the Clausius concept is much nearer to the reinterpretation given by Kirchhoff than to the original Clausius' one (Schöpf, 1984). Here we try to develop the original interpretation in terms of a value concept in connection with some more recent developements. We concentrate on processes in isolated systems, i.e. with given energy. Let us start with a comparison of the entropy concepts of Clausius, Boltzmann and Gibbs. In classical thermodynamics the entropy difference between two states is defined by Clausius in terms of the exchanged heat

$$dS = \frac{d'Q}{T}; \qquad \delta S = S_2 - S_1 = \int_1^2 \frac{d'Q}{T}. \tag{2.39}$$

Here the transition $1 \rightarrow 2$ should be be carried out on a reversible path and $d'Q$ is the heat exchange along this path. In order to define the entropy of a nonequilibrium state we may construct a reversible "Ersatzprozess" connecting the nonequilibrium state with an equilibrium state of known entropy. Let us assume in the following that the target state 2 is an equilibrium state. By standard definition an equilibrium state is a special state of a system with the properties that the variables are uniquely defined, constant in time and remain the same after isolation from the surrounding (compare section 2.1). The state 1 is by assumption a nonequilibrium state, i.e. a state which will not remain constant after isolation. Due to internal irreversible processes, the process starting from state 1 will eventually reach the equilibrium state 2 which is located (macroscopically) on the same energy level. This is due to the condition of isolation which is central in our picture. Now we may apply eq. (2.39) finding in this way the nonequlibrium entropy.

$$S_1(\boldsymbol{y}; E, \boldsymbol{X}, t = 0) = S_{eq}(E, \boldsymbol{X}) - \delta S(\boldsymbol{y}; E, \boldsymbol{X}) \tag{2.40}$$

The quantity δS is the so-called entropy lowering in comparison to the equilibrium state with the same energy. It was introduced by Klimontovich as a measure of organization contained

in a nonequilibrium system (Klimontovich, 1982, 1989, 1990; Ebeling and Klimontovich, 1984; Ebeling, Engel and Herzel, 1990). Several examples were given as e.g. the entropy lowering of oscillator systems, of turbulent flows in a tube and of nonequlibrium phonons in a crystal generated by a piezoelectric device.

We shall assume in the following that the entropy lowering depends on a set of order parameters $\boldsymbol{y} = y_1, y_2, ..., y_n$ as well as on the energy E and on other extensive macroscopic quantities $\boldsymbol{X}$. The equilibrium state is characterized by $y_1 = y_2 = ... = y_n = 0$.

There are some intrinsic difficulties connected with the construction of an "Ersatzprozess"; therefore Muschik (1990) has developed the related concept of an accompanying process. By definition this is a projection of the real path on a trajectory in an equilibrium subspace. Since the entropy is as a state function independent on the path, the concepts "Ersatzprozess" or accompanying process give at least a principal possibility of calculating the nonequilibrium entropy. In practice these concepts work well for nonequilibrium states which are characterized by local equilibrium, which is valid e.g. for many hydrodynamic flows and chemical reactions (Glansdorff and Prigogine, 1971). In more general situations the exact definition of the thermodynamic entropy remains an open question, which is the subject of intensive discussions (Ebeling and Muschik, 1992). Let us consider now another approach which is based on the concept of entropy production. Assuming again that the initial state 1 is a nonequilibrium state, we know from the definition of equilibrium that, after isolation, changes will occur. Under conditions of isolation the energy E will remain fixed, within the natural uncertainties, but the entropy will monotoneously increase due to the second law. Irreversible processes connected with a positive entropy production $P > 0$ will drive the system finally to an equilibrium state located at the same energy surface. In thermodynamic equilibrium, the entropy assumes the maximal value $S_{eq}(E, \boldsymbol{X})$ which is a function of the energy and certain other extensive variables. According to eq. (2.37) the entropy change is a Lyapunov functions and may be obtained by integration of the entropy production over time:

$$\delta S = S_{eq}(E, \boldsymbol{X}) - S(E, t = 0) = \int_1^2 P(t)dt \qquad (2.41)$$

In the special case that production of heat by destruction of mechanical work is the only irreversible process application of eq. (2.41) is quite easy. Since then $P(t)$ is given as the quotient of heat production and temperature a calculation of requires the knowledge of the total mechanical energy which is dissipated. Eq. (2.41) is another way to obtain the entropy lowering and in this way the entropy of any nonequilibrium state. As above we may consider this difference as a measure of order contained in the body in comparison with maximal disorder in equilibrium. Eq. (2.41) suggests also the interpretation as a measure of distance from equilibrium. So far the thermodynamic meaning of entropy was discussed, but entropy is like the face of Janus, it allows other interpretations. The most important of them with respect to statistical physics is the interpretation of entropy as measure of uncertainty or disorder. In the pioneering work of Boltzmann, Planck and Gibbs it was shown that in statistical mechanics

the entropy of a macrostate is defined as the logarithm of the thermodynamic probability W

$$S = k_B \log W \tag{2.42}$$

which is defined as the total number of equally probable microstates corresponding to the given macrostate. Further k_B is the Boltzmann constant. In the simplest case of classical systems, the number of states with equal probability corresponds to the volume of the available phase space $\Omega(A)$ divided by the smallest accessable phase volume h^3 (h - Planck's constant). Therefore the entropy is given by

$$S_{BP} = k_B \log \Omega^*(A), \tag{2.43}$$

$$\Omega^*(A) = \Omega(A)/h^3 \tag{2.44}$$

Here A is the set of all macroscopic conditions. In isolated systems in thermal equilibrium, the available part of the phase space is the volume of the energy shell enclosing the energy surface

$$H(\boldsymbol{q}, \boldsymbol{p}) = E. \tag{2.45}$$

If the system is isolated but not in equilibrium only certain part of the energy shell will be available. In the course of relaxation to equilibrium the probability is spreading over the whole energy shell filling it finally with constant density. Equilibrium means equal probability, and as we shall see, least information about the state on the shell. In the nonequilibrium states the energy shell shows regions with increased probability (attractor regions). We may define an effective volume of the occupied part of the energy shell by

$$S(E, t) = k_B \log \Omega^*_{eff}(E, t), \tag{2.46}$$

$$\Omega^*_{eff}(E, t) = \exp\left(S(E, t)/k_B\right) \tag{2.47}$$

In this way, the relaxation on the energy shell may be interpreted as a monotoneous increase of the effective occupied phase volume. This is connected with a devaluation of the energy.

Let us discuss now in more detail the relation between free energy and work. The energetic basis of all human activities is work, a term which is also difficult to define. The first law of thermodynamics expresses the conservation of the energy of systems. Energy may assume various forms. Such forms of energy as heat or work appear in processes of energy transfer between systems. They may be of different value with respect to their ability to perform work. The (work) value of a specific form of energy is measured by the entropy of the system. As shown first by Helmholtz, the free energy

$$F = E - TS \tag{2.48}$$

represents the amount of energy in a body at fixed volume and temperature which is available for work. Before going to explain this in more detail we go back for a moment to a system with fixed energy and with fixed other external extensive parameters. Then the capacity to

do work (the work value) takes it minimum zero in thermodynamic equilibrium, where the entropy assumes the maximal value $S_{eq}(E, X)$. Based on this property Helmholtz and Ostwald developed a special entropy concept based on the term "value". In the framework of this concept we consider the difference

$$\delta S = S_{eq}(E, X) - S(E, X) \tag{2.49}$$

as a measure of the "value" of the energy contained in the system. In dimensionless units we may define a "lowering of entropy" by

$$Le = [S(E, X) - S(E, X)]/Nk_B \tag{2.50}$$

where N is the particle number. We consider Le as a quantity which measures the distance from equilibrium or as shown above the (work) value of the energy contained in a system. Further the lowering of entropy Le should also be connected with the nonoccupied part of the phase space. As shown above, any nonequilibrium distribution is concentrated on certain part of the energy surface only. Therefore the relaxation to equilibrium is connected with a spreading of the distribution and a decrease of our knowledge on the microstate.

In terms of the phase space volume of statistical mechanics this measure has the following meaning. It gives the relative part of the phase space in the energy shell which is occupied by the system. The second law of thermodynamics tells us that entropy can be produced in irreversible processes but never be destroyed. Since entropy is a measure of value of the energy this leads to the formulation that the distance from equilibrium and the work value of energy in isolated systems cannot increase spontaneously. In other words Le and w are Lyapunov functions expressing a tendency of devaluation of energy.

In order to increase the value of energy in a system one has to export entropy. In this way we have shown, that the meaning of the thermodynamic concept of entropy may be well expressed in terms of distance from equilibrium, of value of energy or of relative phase space occupation instead of the usual concept of entropy as a measure of disorder.

Now let us come back to the free energy, the term introduced into thermodynamics by Helmholtz. As we will shown in detail, the concept of Helmholtz may be interpreted in the way that the total energy consists of a free part which is available for work and a bound part which is not available. A related concept is the exergy, which is of much interest for technical applications. Due to the relation

$$E = F + TS = E_f + E_b \tag{2.51}$$

the energy in a body consists of two parts.

$$E = E_f + E_b; \qquad E_f = F; \qquad E_b = TS \tag{2.52}$$

Correspondingly, the first part $E_f = F$ may be interpreted as that part of the energy, the "free energy", that is available for work. The product of entropy with the temperature $E_b = TS$ may be interpreted as the bound part of the energy. On the other hand due to

$$H = G + TS = H_f + H_b \tag{2.53}$$

it gives also the bound part of the enthalpy (G - being the free enthalpy). From the second law follows as shown in the previous section that under isothermal conditions the free energy is a non-increasing function of time

$$\frac{dF}{dt} \leq 0 \tag{2.54}$$

and that under isobaric-isothermal condition the free enthalpy is non-increasing

$$\frac{dG}{dt} \leq 0 \tag{2.55}$$

The tendency of F and G to decrease is in fact determined by the general tendency expressed by the second law, to devaluate the energy (or the enthalpy) with respect to their ability to do work.

Let us study now the work W performed on a system during a finite transition from an initial nonequilibrium state to a final equilibrium state. Then as we have shown

$$W = \delta F = F_{ne} - F_{eq} \tag{2.56}$$

is the work corresponding to a process when the parameters are changed infinitely slowly along the path γ from the starting nonequilibrium point to the final equilibrium state. This relation is not true, if the parameters are switched along the path γ at a finite rate. At that conditions the process is irreversible and the work W will depend on the microscopic initial conditions of the system and the reservoir, and will, on average exceed the free energy difference (Jarzynski, 1996)

$$\langle W \rangle \geq \delta F = F_{ne} - F_{eq} \tag{2.57}$$

The averaging is to be carried out over an ensemble of transitions (measurements). The difference

$$[\langle W \rangle - W] \geq 0 \tag{2.58}$$

is just the dissipated work W_{dis} associated with the increase of entropy during the irreversible transition.

In recent work Jarzynski (1996) discussed the above relations between free energy and work from a new perspective. The new relation derived by Jarzynski (1996) instead of the inequality (2.57) is an equality

$$\langle \exp[-\beta W] \rangle = \exp[-\beta W] \tag{2.59}$$

where $\beta = 1/k_B T$. This nonequilibrium identity, proven by Jarzynski (1997) using different methods, is indeed surprising: It says that we can extract equilibrium information

$$\delta F = W = -k_B T[\ln\langle \exp(-\beta W) \rangle] \tag{2.60}$$

from an ensemble of nonequilibrium (finite-time) measurements. In this respect eq.(2.60) is an equivalent of eq.(2.22).

2.4   Deterministic Level

Description by variables:

$$\mathbf{x}(\mathbf{t}) = [x_1(t), x_2(t), ..., x_n(t)] \tag{2.61}$$

$$\dot{x}_i(t) = F_i(x_1, ..., x_n(t)), \qquad i = 1, 2, ..., n \tag{2.62}$$

A detailed pictues you will find in the book, also in many available textbooks.

2.5   Stochastic Level of Description

Due to stochastic influences the future state of a dynamical system is in general not uniquely defined. In other words the dynamic map defined by (2.62) is non-unique. A given initial point $x(0)$ may be the source of several different trajectories. The choice between the different possible trajectories is a random event.

Description developed by Paul Langevin (1911):

Add stochastic forces with zero mean value

$$\dot{x}_i = F_i(x) + \sqrt{2D}\xi_i(t) \tag{2.63}$$

where $xi(t)$ is a delta-correlated Gaussian random variable.

$$< \xi(t) > = 0; \qquad < \xi_i(t)\xi_j(t') > = \delta_{ij}\delta(t - t') \tag{2.64}$$

By averaging we find

$$\dot{< x >} = < F_i(x) > \simeq F_i(< x >) \tag{2.65}$$

This way, in average, the deterministic dynamics is reproduced at least approximately.

After all the term trajectory looses its precise meaning and should be supplemented in terms of probability theory. We describe the state of the system at time t by a probability density $P(\boldsymbol{x}, t; \boldsymbol{u})$. Per definition $P(\boldsymbol{x}, t; \boldsymbol{u})d\boldsymbol{x}$ is the probability of finding the trajectory at time t in the interval $(\boldsymbol{x}, \boldsymbol{x} + dx)$. Instead of the deterministic equation for the state we get now a differential equation for the probability density $P(\boldsymbol{x}, t; \boldsymbol{u})$.

Define $\boldsymbol{G}$ as the probability flow vector. Based on the equation of continuity we get

$$\partial_t P(\boldsymbol{x}, t; \boldsymbol{u}) = -\mathrm{div}\boldsymbol{G}(\boldsymbol{x}, t; \boldsymbol{u}) \tag{2.66}$$

In the special case that there are no stochastic forces the flow is proportional to the deterministic field i.e.

$$G_i(\boldsymbol{x}, t, ; u) = F_i(\boldsymbol{x}, t; u)P(\boldsymbol{x}, t; u)$$

Including now the influence of the stochastic forces we assume here *ad hoc* an additional diffusive contribution to the probability flow which is directed downwards the gradient of the probability

$$G_i(\boldsymbol{x}, t; \boldsymbol{u}) = F_i(\boldsymbol{x}, t; \boldsymbol{u})P(\boldsymbol{x}, t; \boldsymbol{u}) - D\frac{\partial}{\partial x_i}P(\boldsymbol{x}, t; \boldsymbol{u}) \tag{2.67}$$

This is the simplest "Ansatz" which is consistent with eq.(2.73) for the mean values. The connection of the "diffusion coefficient" D with the properties of the stochastic force will be discussed later. Introducing eq.(2.5) into eq.(2.66) we get a partial differential equation.

$$\frac{\partial}{\partial t}P(\boldsymbol{x},t;\boldsymbol{u}) = \sum_i \frac{\partial}{\partial x_i}\left[D\frac{\partial}{\partial x_i}P(\boldsymbol{x},t;\boldsymbol{u}) - F_i(\boldsymbol{x},t;\boldsymbol{u})P(\boldsymbol{x},t;\boldsymbol{u})\right] \qquad (2.68)$$

We will use the following notation:
(i) If $x_1,...x_n \to x_1,...,x_f$ are usual mechanical coordinates, we call the equation *Smoluchowski equation* to honour the contribution of Marian Smoluchowski (18.. - 1917).
(ii) If $x_1,...,x_n \to x_1,...,x_f,v_1,...v_f$ represent coordinates and velocities (momenta) we denote the equation as *Fokker-Planck equation*, since Fokker and Planck wrote down the first version. Alternatively we may call the equation *Klein-Kramers equations* after the scientists which formulated the standard form used nowadays.
(iii) In the general case that the meaning of the $x_1,...,x_n$ is not specified at all, we speak about the it Chapman-Kolmogorov equation.
In the literature all these equations are often called the *Fokker-Planck equation* but this is historically not fully correct.

In this way we have found a closed equation for the probabilities. The found stochastic equation is consistent with the deterministic equation (2.62) and will, at least approximately, take into account stochastic influences.

On the basis of a given probability distribution $P(x,t;u)$ we may define now mean values of any function $f(x)$ by

$$\langle f(\boldsymbol{x})\rangle = \int d\boldsymbol{x} f(\boldsymbol{x})P(\boldsymbol{x},t;u).$$

Further we may define the standard statistical expressions as e.g. the dispersion and in particular the mean uncertainty (entropy) which is defined as

$$H = -\langle \log P(\boldsymbol{x},t;u)\rangle \qquad (2.69)$$

The Fokker-Planck equation has a unique stationary solution

$$P_0(\boldsymbol{x};u)$$

which is the target of evolution

$$P(\boldsymbol{x},t;u) \to P_0(\boldsymbol{x};u)$$

There exists a non-negative functonal

$$K(P;P_0) = \langle \log \frac{P(\boldsymbol{x},t;u)}{P_0(\boldsymbol{x};u)}\rangle$$

such that

$$\frac{dK(P;P_0)}{dt} \leq 0$$

This is a very general stochastic inequality which has many special cases.

Let us first study a system with
For systems with overdamped potential dynamics in configuration space and friction

$$\rho = m\gamma_0$$

$$F_i(\boldsymbol{x}, t; u) = -\frac{\partial V(\boldsymbol{x}, t; u)}{\rho \partial x_i}$$

we get the Smoluchowski equations and the solution reads

$$P_0(\boldsymbol{x}; u) = const \exp\left[-\frac{V(\boldsymbol{x}, t; u)}{D\rho}\right]$$

With the Einstein relation

$$D = \frac{kT}{\rho}$$

this gives the Boltzmann distribution.

$$P_0(\boldsymbol{x}; u) = \frac{1}{Q} \exp\left[-\frac{V(\boldsymbol{x}; u)}{k_B T}\right]$$

This gives

$$k_B T K = <v(x)> -U_x(T; u)$$

where U_x is the configurational part of the internal energy defined by

$$U_x = F_x + TS_x; \qquad F_x = k_B T \ln Q; \qquad S_x = -\int dx P(x) \ln P(x)$$

In the case of an hamiltonian dynamics we find the Fokker-Planck-Klein-Kramers equation and the the stationary solution reads

$$P_0(\boldsymbol{x}, \boldsymbol{v}; u) = \frac{1}{Z} \exp\left[-\frac{H(\boldsymbol{x}, \boldsymbol{v}; u)}{k_b T}\right]$$

Then we find the non-negative functonal

$$K(P; P_0) = \langle \log \frac{P(\boldsymbol{x}, v, t; u)}{P_0(\boldsymbol{x}, v; u)} \rangle = \beta(F(t) - F_0)$$

such that

$$\frac{dF(t))}{dt} \leq 0; \qquad F(t) \rightarrow F_0$$

The approach based on the Fokker-Planck equation is the simplest but not the only one. There exists a different approach due to Markov, Chapman and Kolmogorov, which is based on transition probabilities and the idea of a so-called Markov chain.

Let us still underline that the concept of the Markov process is rather a property of the model we apply for the description than a property of the physical system under consideration (Van Kampen, 1981). If a certain physically given process cannot be described in a given state space by a Markov relation, often it may be possible, by introducing additional components, to embed it into a Markov model. This way a non-Markovian model can be converted, by enlargement of the number of variables, into another model with Markovian properties. We note already here, that the basic equation of statistical physics, the Liouville equation which will be introduced in the next Chapter, is of markovian character.

By some manipulation of the Chapman-Kolmogorov equation we get the following equation for the probability density.

$$\frac{\partial P(x,t)}{\partial t} = \int dx' W(x|x') P(x',t) - W(x'|x) P(x,t) \tag{2.70}$$

This equation is called Pauli-equation or master equation since it plays a fundamental role in the theory of stochastic processes. The integration is performed over all possible states x' which are attainable from the state x by a single jump. It is a linear equation with respect to P and determines uniquely the evolution of the probability density. The r.h.s.consists of two parts, the first stands for the gain of probability due to transitions $x' \to x$ whereas the second describes the loss due to reversed events. Eq.(2.70) needs still further explanation by the determination of the transition probabilities per unit time correspondingly to the special physical situation. It will be the subject of chapters 7. and 8. The transition probability is in many cases a quickly decreasing function of the jump $\Delta x = x - x'$. By using a Taylor expansion with respect to Δx and moments of the transition probability one can transform eq.(2.70) to an infinite Taylor series. This is the so-called *Kramers-Moyal expansion*.

$$\frac{\partial P(x,t)}{\partial t} = \sum_1^\infty \frac{(-1)^m}{m!} \sum \frac{\partial^m M(x) P(x,t)}{\partial x_{i_1}...\partial x_{i_m}} \tag{2.71}$$

with

$$M_{i_1...i_m}(x) = \int d\Delta x d\Delta x_{i_1} d\Delta x_{i_m} W(x + \Delta x|x) \tag{2.72}$$

being the moments of the transition probabilities per unit time. According to Pawula there are just two possibilities considering homogeneous Markov processes
(1) All coefficients of the Kramers-Moyal expansion are different from zero.
(2) Only two coefficients in the expansion are different from zero.
In the first case we have to deal with the full master equation. In the latter one the Markovian

process is called difusive, which is of special interest to us, and leads to the following second-order partial differential equation:

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x_i}[M_i(x)P] + \sum_j \frac{\partial^2}{\partial x_i \partial x_j}[M_{ij}(x)P] \tag{2.73}$$

This is a generalization of the Fokker-Planck equation given above. For its solution we need of course initial conditions $P(x, t = 0)$ and boundary conditions which take into account the underlying physics. Writing eq.(**??**) again in the form of a continuity equation (2.97) we find for the vector of the probability flow the components

$$G_i(x,t) = M_i(x)P(x,t) + \sum_j \frac{\partial}{\partial x_i}[M_{ij}(x)P(x,t)] \tag{2.74}$$

The strong mathematical theory of the given stochastic equations was developed by Chapman, Kolmogorov and Feller; therefore one speaks often about the *Chapman - Kolmogorov - Feller equation.* In physics however, this equation was used much earlier by Einstein, Smoluchowski, Fokker and Planck for the description of diffusion processes and Brownian motion respectively (Chandrasekhar, 1943). Due to this original physical relation the coefficients $M_i(x)$ and $M_{ij}(x)$ are often called drift coefficients and diffusion coefficients respectively. Let us still mention that an alternative mathematical foundation of the theory of stochastic processes may be based on the theory of stochastic differential equations (Gichman et al., 1971).
Another large class of Markovian processes contains systems with a discrete state space. This concerns the atomic processes or extensive thermodynamic variables, like e.g. particle numbers in chemical reacting systems. The Pauli equation which was developed originally for the transitions between atomic levels has the form

$$\frac{\partial}{\partial t}P(\boldsymbol{N},t) = \sum [W(\boldsymbol{N}|\boldsymbol{N}')P(\boldsymbol{N}',t) - W(\boldsymbol{N}'|\boldsymbol{N})P(\boldsymbol{N},t)] \tag{2.75}$$

where $\boldsymbol{N}$ is the vector of possible discrete events (population numbers, occupation numbers). As example we refer to the large class of birth and death processes where $\boldsymbol{N}$ are natural numbers which change during one transition by $\Delta N = \pm 1$. Let us still summarize the new tools in comparison with the deterministic models. Obviously the stochastic approach contains more information about the considered systems due to the inclusion of fluctuations into the description. Besides moments of the macroscopic variables it enables us to determine correlation functions, spectra which will give knowledge between the functional dependence of the fluctuational behaviour at different times.
Some physical phenomena can be explained only by taking into account fluctuations. The stochastic approach on a mesoscopic level delivers often more elegant solutions than the microscopic statistical approach. Inclusion of fluctuations of the macroscopic variables does not necessarily enlarge the number of relevant variables but changes only their character by transforming them into stochastic variables. The main difference compared with the deterministic

models is the permeability of separatrices. This statement concerns especially non-chaotic dynamics, for instance if dealing with one or two order parameter. With certain probability stochastic realizations reach (or cross) unstable points, saddle points, and separatrices what is impossible in the deterministic description. Stochastic effects make possible to escape regions of attraction around stable manifolds. Physical situations which make use of that circumstamce are e.g. nucleation or chemical reactions where energetically unfavourable states has to be overwhelmed.

Problem:
Study a (driven) 1D Rayleigh particle without noise
$D = 0$ and with noise:

$$\dot{x} = v \tag{2.76}$$

$$\dot{v} = (a - bv^2)v + \sqrt{2D}\xi(t) \tag{2.77}$$

Find the solution of the Fokker-Planck equation and discuss it.

Chapter 3

Reversibility and Irreversibility, Liouville and Markov Equations

3.1 Boltzmann's kinetic theory

As we stated in the introduction, Boltzmann is the father of statistical physics. He formulated the basic tasks of this scientific discipline: How to derive the macroscopic properties of matter and especially thermodynamic potentials from atomistics and the laws of mechanics. He introduced the new natural constant k_B which connects the basic macroscopic quantity, the entropy S, with the probabilities of microscopic states. Boltzmann's approach was in contradiction to most contemporary views. His arguments and the controversy with Loschmidt, Zermelo and Poincare played a great role for the formation of modern statistical physics.

In classical thermodynamics the entropy difference between two states was defined by Clausius in terms of the exchanged heat $d'Q$ and the temperature T :

$$dS = \frac{d'Q}{T} \tag{3.1}$$

$$\delta S = S_2 - S_1 = \int_1^2 \frac{d'Q}{T} \tag{3.2}$$

Here the transition $1 \rightarrow 2$ should be carried out on a reversible path and $d'Q$ is the heat exchange along this path. Boltzmann first formulated the basic link between Clausius' entropy and probability. In his first work on kinetic theory he introduced the concept of the phase space X of a macroscopic system consisting of N molecules, each of them described by a set of generalized coordinates and momenta:

$$[\boldsymbol{q}, \boldsymbol{p}] = [q_1, q_2, ..., q_f, p_1, p_2, ..., p_f] \tag{3.3}$$

The phase space X is the $2f$-dimensional space of the f coordinates and f momenta which describe the state of one molecule. Here f has in the simplest case of Cartesian coordinates of

the molecule the value 3, including further internal degrees of freedom it may be of the order $5 - 6$. Often this space is denoted as the γ-space of statistical mechanics. The state of one molecule in this space corresponds to a point and the state of the ensemble of all molecules of the body, which is under consideration, is a cloud of points (see Fig. 3.1).
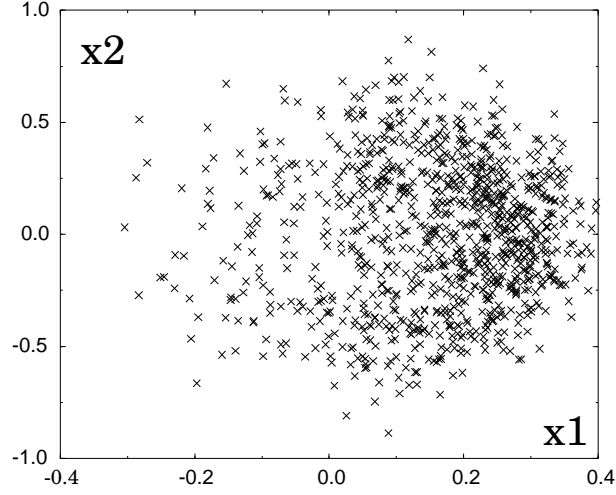

Figure 3.1: A cloud of points in the phase space of molecules corresponding to the state of a macroscopic molecular system.

Let us define, as did already Boltzmann, the function $f(\boldsymbol{q}, \boldsymbol{p}, t)$ as the density of the points in the γ-space. Boltzmann concentrated on dilute gases and in this case the molecules and their corresponding points are independent. Due to this we may interpret the density as a probability to find at time t, some molecule represented by a point at $\boldsymbol{q}$ and $\boldsymbol{p}$; more precise we have to consider not phase points but volume elements $d\boldsymbol{q}d\boldsymbol{p}$ in the phase space. We consider $f(\boldsymbol{q}, \boldsymbol{p}, t)$ as dimensionless and take into account that the volume element in the phase space $d\boldsymbol{q}d\boldsymbol{p}$ has the dimension of an action to the power of the space dimension. Therefore we have chosen Plancks constant h^3 as a normalization factor. Note, that we we have chosen as the most natural unit of action Planck's constant, which was of course not yet known to Boltzmann. With our choice $f(\boldsymbol{q}, \boldsymbol{p}, t)$ is dimensionless and

$$f(\boldsymbol{q}, \boldsymbol{p}, t)\frac{d\boldsymbol{q}d\boldsymbol{p}}{h^3} \tag{3.4}$$

can be interpreted as the density (probability) of finding at time t a point in the interval $d\boldsymbol{q}d\boldsymbol{p}$. The normalization is assumed to be

$$N = \int \frac{d\boldsymbol{q}d\boldsymbol{p}}{h^3} f(\boldsymbol{q}, \boldsymbol{p}, t) \tag{3.5}$$

where N is the total number of molecules in the gas. In 1866, Boltzmann was able to derive an expression for the distribution function for the special case of thermal equilibrium $f^{eq}(\boldsymbol{q}, \boldsymbol{p})$. Instead of repeating the derivation let us simply state the central ideas. We consider two particles with the states $\boldsymbol{q}, \boldsymbol{p}$ and $\boldsymbol{q}_1, \boldsymbol{p}_1$ before a collision. Assuming that $\boldsymbol{q}', \boldsymbol{p}'$ and q_1', p_1' are the corresponding states after the collision, we expect that the products of probabilities before and after the collision are equal

$$f^{eq}(\boldsymbol{q}, \boldsymbol{p}) f^{eq}(\boldsymbol{q}_1, \boldsymbol{p}_1) = \tag{3.6}$$

$$f^{eq}(\boldsymbol{q}', \boldsymbol{p}') f^{eq}(\boldsymbol{q}_1', \boldsymbol{p}_1') \tag{3.7}$$

where both sets of states are connected by the equations of motion for the collisions. The products in Eq. (3.6) express the independence of the molecules far before and after the collision. Equation (3.6) may be rewritten as

$$\ln f^{eq}(\boldsymbol{q}, \boldsymbol{p}) + \ln f^{eq}(\boldsymbol{q}_1, \boldsymbol{p}_1') \tag{3.8}$$

$$= \ln f^{eq}(\boldsymbol{q}', \boldsymbol{p}') + \ln f^{eq}(q_1', p_1') \tag{3.9}$$

Equation (3.7) suggests that the function $\log f^{eq}(\boldsymbol{q}, \boldsymbol{p})$ depends only on invariants of motion. Assuming that the relevant invariant is the Hamiltonian and that the dependence is linear, we arrive at

$$\ln f^{eq}(\boldsymbol{q}, \boldsymbol{p}) = -\beta H(\boldsymbol{q}, \boldsymbol{p}) \tag{3.10}$$

where β is a constant. For the identification of β we may use known relations from the thermodynamics of ideal gases. From Eq. (3.8) we obtain for the mean kinetic energy

$$\langle E_{kin} \rangle = \langle \frac{\boldsymbol{p}^2}{2m} \rangle = \frac{3}{2\beta} \tag{3.11}$$

Comparing this with the energy of ideal gases the constant β can be identified with the reciprocal temperature multiplied with a constant.

$$\beta = \frac{1}{k_B T}$$

$$k_B = 1.381 \cdot 10^{-23} J/K \tag{3.12}$$

Boltzmann's constant k_B is a universal constant which characterizes the connection between microphysics and macrophysics. The fact that in statistical physics a new universal constant appears, makes clear that statistical physics is indeed a new physics in comparison with microphysics. This situation corresponds to the philosophical idea that the whole is more than the sum of its parts. Boltzmann's constant stands for emergent properties of macrosystems.

This way we get finally for point particles in a potential field the famous *Maxwell-Boltzmann distribution*

$$f^{eq}(\boldsymbol{q}, \boldsymbol{p}) = const \exp\left(-\frac{\boldsymbol{p}^2/2m + U(q)}{k_B T}\right) \tag{3.13}$$

By using the probabilistic concepts discussed above, Boltzmann introduced also a new function of the probabilities which possesses very interesting properties:

$$H_B = -\int \frac{d\boldsymbol{q}d\boldsymbol{p}}{h^3} f(\boldsymbol{q}, \boldsymbol{p}, t) \tag{3.14}$$

$$\cdot \ln f(\boldsymbol{q}, \boldsymbol{p}, t). \tag{3.15}$$

In fact, he used the opposite sign for H_B in his original definition; we introduced the "minus" to be consistent with the standard notation in mathematics and informatics. Indeed a similar function (with the minus sign) was suggested already in the eighteenth century by the mathematician DeMoivre for the characterization of the mean uncertainty in the outcome of games. In modern times Claude Shannon founded the information theory on an H-function. In any case, Boltzmanns H_B measures the mean uncertainty of the location of the molecules in the phase space. Later we shall come back to this point several times. Following the basic postulate of Boltzmann the H_B-function is connected with the thermodynamical entropy by the relation

$$S = k_B H_B \tag{3.16}$$

At least in equilibrium this assumption proves to be correct since introducing Eq. (3.9) into Eqs. (3.12-13) leads to

$$S = -k_B N[\ln(n\Lambda^3) + const] \tag{3.17}$$

Here Λ is the thermal De Broglie wave length defined by

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

The entropy obtained this way, corresponds up to a constant to the standard expression from equilibrium thermodynamics. In the phenomenological thermodynamics the expression for the entropy contains the so-called Sacur-Tetrode constant, which is estimated from experiments. In the statistical theory the new constant is given explicitly in a natural way by the normalization procedure; remarkably this constant depends on h. Originally, Boltzmann's hypothesis was essentially based on a theorem on the time evolution of H_B. Indeed, he succeeded in deriving first an equation for $f(\boldsymbol{q}, \boldsymbol{p}, t)$ which has the form of an integro-differential equation. For simplicity we restrict ourselves from now to the case that the distribution does not depend on $\boldsymbol{q}$, which is true for spatially homogeneous systems. Then we get according to Boltzmann

$$\frac{\partial f(\boldsymbol{p}, t)}{\partial t} = I[f(\boldsymbol{p}, t)] \tag{3.18}$$

with a certain nonlinear functional I of the distribution function:

$$I[f(\boldsymbol{p}, t)] = \int \sigma \left[f(\boldsymbol{p}')f(\boldsymbol{p}_1') - f(\boldsymbol{p})f(\boldsymbol{p}_1) \right] d\boldsymbol{p}' d\boldsymbol{p}_1' d\boldsymbol{p}_1 \tag{3.19}$$

where σ is the so-called cross section. We see immediately that the equilibrium distribution (3.9) is a stationary solution of Eq. (3.15). The concrete form of this functional is not essential for our consideration, for smaller deviations from equilibrium we may approximate it in the form

$$I[f(\boldsymbol{p}, t)] \simeq -\nu \left[f(\boldsymbol{p}, t) - f^{eq}(\boldsymbol{p}, t)\right] \tag{3.20}$$

The physics behind this expression is the plausible assumption that the effect of collision occuring with the frequency ν is proportional to the deviation from equilibrium. By using this so-called relaxation time approximation we immediately find a solution of the form

$$f(p, t) = f^{eq}(p) + \exp(-\nu t)[f(p, 0) - f^{eq}(p)]. \tag{3.21}$$

This result means physically that there is an exponential relaxation of all deviations from the Maxwell-Boltzmann distribution. By introducing (3.18) into the formula for the entropy

$$S = -k_B \int (d\boldsymbol{q} d\boldsymbol{p}/h^3) f(\boldsymbol{q}, \boldsymbol{p}, t) \ln f(\boldsymbol{q}, \boldsymbol{p}, t), \tag{3.22}$$

we may show that

$$\delta S(t) = S_{eq} - S(t) \tag{3.23}$$

is non-negative and is a monotonously decreasing function, giving

$$\delta S(t) \geq 0 \tag{3.24}$$

and

$$\frac{d}{dt} \delta S(t) \leq 0. \tag{3.25}$$

As shown by Boltzmann, one may prove this directly from eq. (3.15-16) by using several tricks. Therefore, $\delta S(t)$ is a Lyapunov function; it follows that $S(t)$ always increases. This is in full agreement with the second law of thermodynamics. It was exactly this point, which Boltzmann considered as the main success of his theory, that was later the target of the heavy attacks from other experts as Poincare, Loschmidt and Zermelo. Before we explain this point in more detail, let us first discuss one essential generalization of Boltzmann's approach, which is due to Gibbs. The most essential restriction of Boltzmann's theory was the assumption of weak interactions between the particles. This assumption could be removed by the great American theoretician Josiah Willard Gibbs (1839-1903) who published in 1902 a fundamental book *"Elementary Principles in Statistical Mechanics"*. Gibbs considered a more general class of macroscopic systems. He introduced a high-dimensional phase space, the so-called Γ-space, which is given by all the $3N$ (or fN respectively) coordinates $q_1, ..., q_{3N}$ and the $3N$ momenta $p_1, ..., p_{3N}$ of the macroscopic system. Gibbs' generalization of the entropy to interacting systems of point-like molecules reads:

$$S_G = -k_B \int (d\boldsymbol{q} d\boldsymbol{p}/h^{3N}) \rho(\boldsymbol{q}, \boldsymbol{p}) \cdot \ln \rho(\boldsymbol{q}, \boldsymbol{p}) \tag{3.26}$$

where $\rho(\boldsymbol{q}, \boldsymbol{p})$ is the normalized probability density in the $6N$-dimensional phase space. The Gibbs expression includes all interaction effects which in general lead to a decrease of the value of the entropy in comparison to the ideal gas. For the special case of equilibrium systems with fixed energy E the probability density is assumed to be constant in a shell around the surface

$$H(q_1, ..., q_{3N}, p_1, ..., p_{3N}) \simeq E. \tag{3.27}$$

Gibbs calls this the microcanonical distribution or the microcanonical ensemble. In principle Gibbs assumption goes back to Boltzmann's hypothesis, that the trajectory fills the whole energy shell in a uniform way. We will come back to this idea of ergodicity in the next section. Boltzmann assumed that in the case of equal probabilities of the microstates the entropy of the corresponding macrostate is the logarithm of the thermodynamic probability

$$S_{BP} = k_B \ln W. \tag{3.28}$$

where W is defined as the total number of equally probable microstates corresponding to the given macrostate. Strictly speaking, the first explicit writing of formula eq.(3.28) is due to Planck, therefore we will speak sometimes about the Boltzmann-Planck entropy. As we see, the Gibbs' expression for the entropy is for a constant probability density (microcanonical distribution) in full agreement with the Boltzmann-Planck formula

$$S_G(E, V) = k_B \ln \Omega^*(E, V) : \tag{3.29}$$

$$\Omega^*(E, V) = W = \Omega(E, V)/h^{3N}.$$

Here $\Omega(E)$ is the volume of the energy shell. We assume as earlier, that Planck's constant defines the appropriate unit cell, in order to make the argument of the log dimensionless. As above W is the number of equally probable microstates in the energy shell. All these arguments will be explained in much more detail in Chapter 4. In principle, with expressions for the entropy either in the Boltzmann-Planck or in the Gibbs form, we reached already at our aim, to derive thermodynamics from microphysics. However, the solution is not as simple, there remain open problems.

Boltzmann's first paper on the connection between mechanics and thermodynamics appeared in 1871; it had the remarkable title *"Analytical Proof of the Second law..."*. In a later (main) paper which appeared in 1872, he worked out his arguments in more detail and presented further results. However in 1876 Boltzmann's teacher and colleague Loschmidt published a serious objection against Boltzmann's theory, which became known as the Loschmidt's paradox. Loschmidt considered a gas in a box with completely plane elastic surfaces. During the time evolution of this system Boltzmann's H-function at subsequent times should form a nondecreasing time series

$$H_B(t_1) \leq H_B(t_2) \leq ... \leq H_B(t_n). \tag{3.30}$$

Loschmidt then proposed the following "Gedankenexperiment". Consider at certain time t_n an inversion of all the velocities of the molecules. Corresponding to the reversibility of the laws of

mechanics we would observe a backward trajectory leading to a decreasing H-function.

$$H_B(t_n) \geq H_B(t_{n-1}) \geq ... \geq H_B(t_1). \tag{3.31}$$

However this is in clear contradiction to Boltzmann's H-Theorem and to the second law. The next critical objection against Boltzmann's theory was based on the theorem of Poincare about the *"quasi-periodicity of mechanical systems"* published in 1890 in the famous paper *"Sur le probleme de trois corps les equations de la dynamique"*. 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, a student of Planck, showed in 1896 in a paper in the *"Annalen der Physik"* that Boltzmann's H-theorem and Poincares recurrence theorem are contradictory. On the basis of these arguments Chandrasekhar (1943) concluded that *"a process would appear to be irreversible (or reversible) according as whether the initial state is characterized by a long (short) average time of recurrence compared to the time during which the system is under observation"*. Poincare himself was very critical about Boltzmann's work, which he believed to be completely wrong. At that time, Poincare could not know that he had already created the tools for the solution to that deep controversy. The clue was the concept of the instability of trajectories, developed by Poincare in 1890. Recent results on chaotic dynamics lead us to revise Poincare's conception (Prigogine, 1980, 1989, Petrosky & Prigogine, 1988; Gaspard, 1998; Dorfman, 1999, Hoover, 2001). Most systems of statistical mechanics such as systems of hard spheres are characterized by positive Lyapunov exponents, which implies the existence of a finite time horizon. As a result, the concept of classical trajectories is lost for long times, and the existence of a Poincare's recurrence time becomes irrelevant for times much longer than the Lyapunov time (Prigogine, 1989).
Other quite different, but indeed convincing arguments in favour of Boltzmann's approach are based on computer simulations. First in 1957 Alder and Wainwright started to simulate the dynamics of molecules (beginning with hard core models) on a computer. Now this method is getting more and more a central part of statistical physics with very fruitful implications (Hoover, 2001). This can be said also on the closely related Monte Carlo method (Binder, 1987). Computer simulations based on molecular dynamics are most useful to clarify the relations between the irreversibility and molecular dynamics, as well as between probability and fluctuations (Marechal and Kestemont, 1987; Hoover, 1988, 2001; Morosov et al., 2001; Norman & Stegailov, 2002).

3.2 Probability measures and ergodic theorems

Boltzmann's approach to introduce probabilities into physics has proven to be one of the most fruitful ideas of science and yet, in his day, Boltzmann was heavily attacked by mathematicians and physicists. The reasons for these attacks were, that Boltzmann was forced to introduce some probabilistic assumptions which were in contradiction to the principles of mechanics. In an effort to place his theory on on firm ground, Boltzmann founded the subject of ergodic

theory. The aim of ergodic theory is to derive probabilities from the study of the flow of trajectories (Balescu, 1963; Arnold & Avez, 1968; Sinai, 1977).

In order to explain the key point of Boltzmann's idea, let us first remind several notations and results obtained in the framework of the classical mechanics of Hamiltonian systems. We consider a Hamilton dynamics which is defined by a scalar function H, called the Hamiltonian, which is defined on a space of f coordinates $q_1, ..., q_f$ and f momenta $p_1, ..., p_f$:

$$H(q_1, ..., q_f, p_1, ..., p_f). \tag{3.32}$$

The equations of motions of our Hamiltonian dynamics are

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \qquad \frac{dp_i}{dt} \tag{3.33}$$

$$= -\frac{\partial H}{\partial q_i}. \tag{3.34}$$

By integration of the Hamiltonian equations at given initial state $\boldsymbol{q}(t), \boldsymbol{p}(t), i = 1, ..., f$ we may calculate the future state at $t + \delta t$ in a unique way. A Hamiltonian system given by (3.32-3.34) is either "integrable" or "non-integrable" dependent on the behavior of the integrals of motion

$$I_k(q_1, ...q_f, p_1, ..., p_f) = C_k \tag{3.35}$$

where the C_k are certain constants. The Hamiltonian system is called "integrable" if there exist f constants of motion which are single valued differentiable (analytic) functions. These f functions must be independent of each other and exist globally, i.e. for all allowed values of the coordinates and momenta. As well known, a mechanical systems with f degrees of freedom has in total $2f - 1$ integrals of motion (3.35). This expresses just the uniqueness of the trajectory. Namely, if $q_1(t), ...q_f(t), p_1(t), ..., p_f(t)$ are given explicitly as functions of time and the initial values, one may (in principle) exclude the time and find this way $f - 1$ relations of type of eqs.(3.35). For integrable systems exactly f of these integrals are well defined smooth functions and each of them defines a smooth surface in the phase space. The f single-valued constants of motion restrict the $2f$-dimensional phase space to an f-dimensional surface which one can prove to be an f-dimensional torus. Therefore the solution of (3.30) can be expressed in terms of f cyclic variables (angle variables) and f action variables. The Hamilton-Jacobi equation corresponding to eq.(3.34) possesses a global solution. As examples of "integrable" systems we may consider for $f = 1$ the linear oscillator and for $f = 2$ the Kepler problem. For the linear oscillator the constant of motion is the energy $H(q, p) = E$, correspondingly, the motion is restricted to an ellipse. For the Kepler problem the constants of motion are the Hamiltonian itself and the angular momentum. Other examples of integrable high-dimensional systems are chains of coupled harmonic oscillators. In connection with the great importance of coupled oscillators to many branches of physics as e.g. solid state theory, these systems were carefully studied and we arrived nearly at a full understanding. However linear coupling is just

a theoretical model and cannot be considered as a realistic model for the actual interactions in many-body systems. Therefore the main interest of statistical physics is devoted to systems with nonlinear interactions as e.g. hard-core and Lennard-Jones interactions. For such complicated systems, however, theoretical results for $f \gg 1$ are very rare.

A well-studied nonlinear problem of high dimension is the linear chain of Toda oscillators (Toda, 1981, 1983), a system of $N = f$ equal masses moving in a 1-d phase space. In equilibrium all of the masses are situated at their rest positions with mutual distances fixed at certain equilibrium values. The interactions are given by the strong anharmonic potentials:

$$V(r) = \frac{a}{b} \left[\exp(-br) - 1 + ar \right]. \tag{3.36}$$

Here r is the deviation from the equilibrium distance between two of the masses. The forces derived from this potential tend to a constant for expansions much larger than the equilibrium distance, and are exponentially increasing for strong compressions with respect to the equilibrium position. Closely related is the exponential potential which is purely repulsive exponential potential

$$V(r) = A \exp(-br).$$

In the limit $b \to \infty$, $(ab = const)$ we get the well known hard core forces which are zero for expansions and infinitely strong for compressions. Let us mention another potential, the Morse potential, which is also closely related to the Toda potential. The Morse potential, which is defined as the difference of two exponential potentials (with different sign) shows an attracting region similar as the Lennard-Jones potential. The Morse potential which possesses very interesting properties was treated in several recent papers (Dunkel et al., 2001, 2002; Chetverikov & Dunkel, 2003; Chetverikov et al., 2004, 2005). Here we consider only the simpler Toda potential. In the static equilibrium state of the chain, all the molecules are at rest in equidistant positions and the total energy is zero. By a collision we may accelerate a mass at the border of the system and introduce in this way kinetic energy which will run in form of an excitation through the system. In a thermal regime we may excite even a whole spectrum of excitations (Bolterauer & Opper, 1981; Jenssen, 1991; Jenssen & Ebeling, 1991, 2000). In the case of a purely linear coupling we know all about these excitations: We will observe sinusoidal oscillations and waves, acoustical and optical phonons etc.. Eventually local excitations i.e. wave packets will be observed which however show strong dispersion. In other words local excitations are not stable in linear systems. In the case of Toda interactions however these excitations are stable, there exist soliton solutions which are based on the integrability of the Toda system. The strong interest in local excitations of soliton type is especially inspired by the theory of reaction rates (Ebeling and Jenssen, 1988, 1991, Hänggi et al., 1990). In the context considered here, the Toda systems serve as an example of integrable many-particle systems. It is just the special type of the interactions which allows an analytical treatment of the equations of motion. Now we are going to consider the dynamics and the integrals of motion of this system. We study a uniform chain of masses at the positions y_n which are connected to their

nearest neighbors by Toda springs with the nonlinear spring constant b. The Hamiltonian reads

$$H = \sum_n \frac{p_n^2}{2m} + \frac{a}{b} \left[\exp\left(-b(y_{n+1} - y_n) \right) - 1 + a(y_{n+1} - y_n) \right] \tag{3.37}$$

For an infinite uniform chain $(-\infty < n < +\infty)$ Toda (1981, 1983) found the integrals of motion

$$\exp\left[-b(y_{n+1} - y_n) \right] - 1 = \sinh^2 \chi \, \mathrm{sech}^2 \cosh\left(\chi n - \sqrt{ab/m} \sinh \chi t \right), \tag{3.38}$$

corresponding to the soliton energy

$$E^s = \frac{2a}{b} \left(\sinh \chi \cosh \chi - \chi \right). \tag{3.39}$$

The soliton corresponds to a wandering local compression of the lattice with spatial "width" χ^{-1}. The quantity

$$\tau = \left((ab/m)^{1/2} \sinh \chi \right)^{-1} \tag{3.40}$$

defines a characteristic excitation time of a spring during soliton passage (Toda, 1983, Ebeling & Jenssen, 1988, 1991). The energy of a strongly localized soliton satisfying the condition

$$\frac{\sinh^2 \chi}{\chi} \gg 1 \tag{3.41}$$

reads according to eq.(3.35)

$$E^s \simeq \frac{2a}{b} \sinh^2 \chi. \tag{3.42}$$

In this way we have demonstrated that there exists indeed a class of many-particle systems which are integrable. However, integrability is connected always with rather special interactions. In our example most variations of the Toda law (as e.g. the Morse interaction law) destroy the integrability. An interesting property of the Toda system is, that all statistical functions according to the Gibbs theory may be exactly calculated (Toda & Saitoh, 1983). The question however, whether this completely integrable system will assume a thermodynamic equilibrium in the limit of long time, remains completely open. The situation changes drastically if we add a small coupling to a thermal heat bath (Jenssen & Ebeling, 2000). Then we have no problems with irreversibility since the heat bath drives our system to an equilibrium state with exactly known properties. We see that the coupling to a heat bath is at least one possible solution of the irreversibility problem.

We consider now more general many-particle systems in physical space obeying classical mechanics, assuming nonlinear interactions of Lennard-Jones or Morse type. Then the integrals of motion can be divided into two kinds, isolating and nonisolating ones. Isolating integrals define a connected smooth surface in the phase space, while nonisolating integrals are not

defining a smooth surface. The phase trajectory is a cross-section of isolating integrals defining a surface. In this way the cross section of isolating integrals defines that part of the phase space which is filled by trajectories. Boltzmann's hypothesis stated that for statistical-mechanical systems the energy surface

$$H(q_1, ...q_f, p_1, ..., p_f) = E \tag{3.43}$$

is the only isolating integral of motion. Further Boltzmann stated that in the course of time the trajectory will fill the whole energy surface and will come close to any point on it. Further Boltzmann stated that in thermodynamic equilibrium the time average of given phase functions $F(q_1, ...q_f, p_1, ..., p_f)$ exists which is defined by

$$\langle F(q_1, ..q_f, p_1, ..., p_f) \rangle = lim_{T \to \infty} \frac{1}{T} \int_t^{t+T} dt' \tag{3.44}$$

$$F(q_1(t'), ..q_f(t'), p_1(t'), .., p_f(t')) \tag{3.45}$$

For stationary processes, the time average will not depend on the initial time t. However it may possibly depend on the initial state. The state space is called connected (nondecomposable) if it cannot be decomposed into two parts having different time averages. This property guarantees the independence on the initial state of the averaging. The dynamics is called mixing if the average of a product of two phase function equals the product of the averages

$$\langle F(q_1, ...q_f, p_1, ..., p_f)G(q_1, ...q_f, p_1, ..., p_f) \rangle \tag{3.46}$$

$$= \langle F(q_1, ...q_f, p_1, ..., p_f) \rangle \tag{3.47}$$

$$\langle G(q_1, ...q_f, p_1, ..., p_f) \rangle. \tag{3.48}$$

A system is expected to have this property if the trajectories are well mixed. Boltzmann considered the time average as a theoretical model for the result of a measurement of the physical quantity F. Further Boltzmann introduced an ensemble average as the integral over the energy surface

$$\langle F(q_1, ..q_f, p_1, .., p_f) \rangle = \int_{E-\Delta/2 \leq H \leq E+\Delta/2} dq_1..dq_f dp_1..dp_f \tag{3.49}$$

$$F(q_1, ..q_f, p_1, .., p_f). \tag{3.50}$$

Here the integral is to be extended over a thin sheet around the energy surface. The finite width Δ of the surface was introduced for mathematical convenience, physically it may be considered as an uncertainty of the energy measurement. The final part of Boltzmann's so-called ergodic hypothesis (which is formulated here in a more recent notation) states, that time and ensemble averages may be identified, i.e.

$$\langle F(q_1, ...q_f, p_1, ..., p_f) \rangle_t = \tag{3.51}$$

$$\langle F(q_1, ...q_f, p_1, ..., p_f) \rangle_s \tag{3.52}$$

In other words, the result of measurements of F (the time average) may be predicted on the basis of an ensemble averaging. So far there is no general proof of this statement for the case of arbitrary interactions. The modern theory has shown, however, that there are indeed many-body systems, as Sinai's billiard which possess the properties stated hypothetically by Boltzmann. We will see later that ergodicity is related to the chaotic character of the motion of complex Hamiltonian systems. This means, that the practical predictability is limited, in spite of the fact that the initial conditions (if there are known exactly) fully determine the future states. Before we go to a discussion of this fundamental relation, let us first generalize the notation of ergodicity following the work of Birkhoff and others (Ruelle, 1987; Steeb, 1991). A dynamical system is called ergodic if

- for phase functions $F(q_1, ...q_f, p_1, ..., p_f)$ the time average is well defined and,

- a probability measure $\rho(q_1, ...q_f, p_1, ..., p_f)$ exists (called also invariant density) such that

$$\langle F(q_1, ...q_f, p_1, ..., p_f)\rangle_t = \tag{3.53}$$
$$\langle F(q_1, ...q_f, p_1, ..., p_f)\rangle_s. \tag{3.54}$$

The ensemble average used in this condition is defined as

$$\langle F(q_1, ...q_f, p_1, ..., p_f)\rangle_s = \int dq_1..dq_f dp_1..dp_f \tag{3.55}$$
$$F(q_1, .., q_f, p_1, .., p_f)\rho(q_1, .., q_f, p_1, .., p_f). \tag{3.56}$$

Let us conclude this section with a few general remarks about the ergodicity problem: The works of Boltzmann, Gibbs and the Ehrenfests raised the ergodicity problem: to find conditions under which the result of measurements on many-body systems may be expressed by probability measures. Since Boltzmann, Gibbs and Ehrenfest, the subject of ergodic theory was primarily the domain of mathematicians. In 1931 Birkhoff proved an ergodic theorem showing the necessary and sufficient condition for an ergodic behavior of dynamic systems. Nevertheless Birkhoff's result did not close the problem, since for the complex time evolutions which occur in many-body Hamiltonian systems, ergodicity remains a property which is difficult to prove. However on the positive side of the ledger is, that ergodic systems exist indeed, as Sinai's billiard. Sinai has shown in a remarkable paper, that systems consisting of two or more hard spheres enclosed in a hard box are ergodic. From this example as well as from other investigations we know that ergodicity is closely connected with the instability of complex mechanical systems, i.e. with the chaotic character of their dynamics. Very important contributions to this field of research we owe to the early work of Krylov and Born. The main idea of the investigation pioneered by their work is the following: Due to the instability of the motion in phase space the trajectories are becoming very complex. This leads to the mixing character of the trajectories and to integrals of motion which are nonisolating. We mention also that this view is supported by the simulations of the N-particle dynamics by means of powerful computers.

So far a complete solution of the problem of ergodicity is still missing, but anyhow we may state that our understanding of ergodicity has much increased since the times of Boltzmann, Gibbs, Ehrenfest and Birkhoff.

3.3 Dynamics and probability for one-dimensional maps

The most simple dynamical systems, which already show a whole universe of beautiful phenomena including statistical and thermodynamical aspects are 1-dimensional maps (Schuster, 1984, Lasota & Mackey, 1985; Anishchenko, 1989; Ebeling, Steuer & Titchener, 2001). Let us first consider a 1-dimensional map $\boldsymbol{T}$ defined by the iteration

$$\boldsymbol{T}: \qquad x(t+1) = f(x(t)). \tag{3.57}$$

The state $x(t)$ is a point on the one-dimensional x-axis or of certain interval on it. The time t is an integer

$$t = 0, 1, 2, 3.....$$

The trajectory $x(t)$ forms a set of points, one point for each integer time. Let us consider for example the famous logistic map (Fig. 3.2)

$$x(t+1) = rx(t)[1 - x(t)] \tag{3.58}$$

and the tent map (Fig. 3.2)

$$x(t+1) = rx(t) \qquad if \qquad x \leq 1/2$$

$$x(t+1) = r(1 - x(t)) \qquad if \qquad x \geq 1/2 \tag{3.59}$$

Both these examples which map the interval $[0, 1]$ into itself depend on *one* parameter only. The careful study of the dependence of the trajectories $x(t)$ on the value of these parameters, which was pioneered by Feigenbaum, Grossmann and Thomae in the 1970's led us to deep insights. One can get a nice overview about the map by plotting the points generated by 100 interactions in dependence on the r - parameter. Let us give now an elementary consideration of the bifurcation scenario of our nonlinear map (3.49) (see e.g. Holden, 1986). In the region $0 < r < 1$ the state $x = 0$ is stable and the formal solution $x = 1 - (1/r)$ makes no sense for $r < 1$. At $r = 1$ we observe an exchange of stability. The state $x = 0$ is getting unstable and a stable stationary state $x = 1 - (1/r)$ appears. At $r = r_1 = 3$ the stable state $x = 1 - (1/r)$ loses stability and a stable 2-cycle flipping between the states x_2 and x_3 with

$$x_3 = rx_2(1 - x_2), \qquad x_2 = rx_3(1 - x_3) \tag{3.60}$$

is born. At $r = r_2 = 1 + \sqrt{6} = 3.449...$ the two branches of the 2-cycle lose stability and a stable 4-cycle is created. This procedure is continuing in an infinite sequence of bifurcations
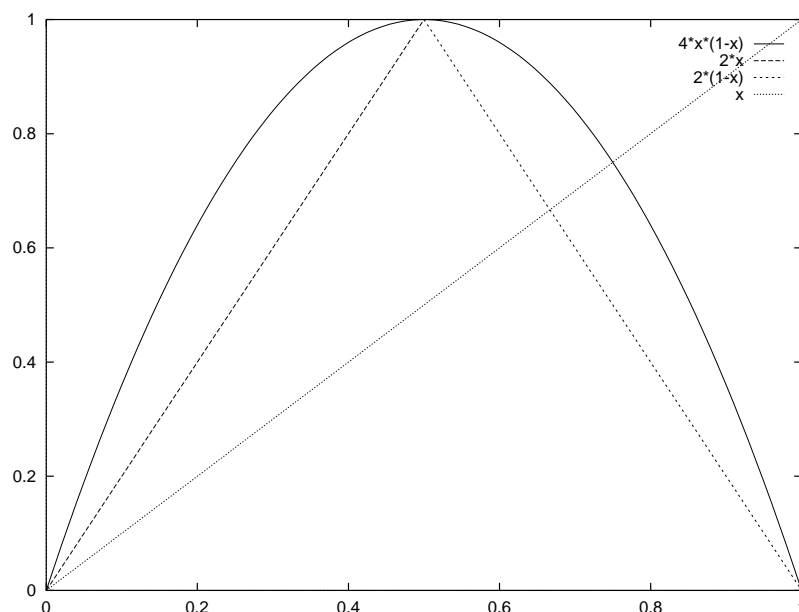
Figure 3.2: Representation of the logistic map for $r = 4$ (a solid line) and the tent-map for $r = 2$ (a dashed line).

occurring at the parameter values

$$r_3 = 3.544090, \qquad r_4 = 3.564407 \qquad\qquad (3.61)$$
$$r_5 = 3.568759, \qquad r_6 = 3.569692, ... \qquad\qquad (3.62)$$

The sequence of period-doubling bifurcations appears to converge to a limit

$$r_\infty = 3.569946...$$

in geometric progression

$$r_k = r_\infty - cF^{-k} \qquad if \qquad k \to \infty \qquad\qquad (3.63)$$

with

$$c = 2.6327..., \qquad F = 4.669202...$$

This behavior was already in 1975 noted by Feigenbaum, who found also - what is most important - that for a very large class of maps, the constant F has the same value. Honoring Feigenbaums pioneering work, the constant F is now named the universal Feigenbaum constant. Let us continue now the bifurcation analysis and proceed to the region $r_\infty < r < 4$. We find there a chaotic behavior of the orbits except for an infinite number of small windows of r-values for which there exist a stable m-cycle. The first such cycles which appear beyond r_∞ are of even period. Next, odd cycles appear as e.g. a 3-cycle at $r = 3.828427$ which stays stable up

to $r = 3.841499$. Then a 6-cycle follows and one observes further period doublings. Outside the window there are no stable periodic orbits although there is an infinite number of unstable cycles. The most chaotic case is reached at $r = 4$. A quantitative way to describe the chaotic behavior in the region $r > r_\infty$ is the Lyapunov exponent defined in section 2.5. In our simple case of 1-d maps the Lyapunov exponent is defined as the time average of the logarithmic slope

$$\lambda = \langle \phi(x(t)) \rangle_t \tag{3.64}$$

where

$$\phi(x) = log|df(x)/dx| \tag{3.65}$$

Following an orbit of the system we may write

$$\lambda = lim_{n \to \infty} \cdot \frac{1}{n} \sum_{k=1}^{n} \log |df/dx|_{x=x_k} \tag{3.66}$$

Except for a measure of value zero, λ is independent of the starting point. According to the definition of chaos in section 2.5 we say in the case $\lambda > 0$ that the orbit is chaotic. Stable orbits as fixed points and limit cycles are characterized by $\lambda < 0$. Lyapunov exponents for the logistic map in dependence on the r-parameter were calculated for the interval where chaos is observed in several papers (see e.g. Ebeling, Steuer & Titchener, 2001).

There is no need here to discuss the bifurcation behavior of the tent map eq.(3.50) in the same detail. Let us just mention that the interesting interval is here $1 < r < 2$. So far we have seen only an interesting bifurcation picture but no connection to the problems of statistical thermodynamics and stochastics, which are all connected with certain probabilities. We shall show now, how probabilities and thermodynamic quantities come into play. Let us consider for example again the logistic map in the case that all the orbits of the system are chaotic at the given value of r (e.g. $r = 4$). We will show that in this case probability may be introduced in a natural way (Lauwerier, 1986). The invariant distribution $p(x)$ is defined by the normalized probability $p(x)dx$ of finding an image $T : x$ in the interval $(x, x + dx)$. The normalization condition reads

$$\int p(x)dx = 1. \tag{3.67}$$

For simplicity we consider only unimodal maps on the interval $0 \le x \le 1$; then any x has at most two pre-images y and z. The probability to find x in the interval $(x, x + dx)$ should equal the sum of finding the pre-images y and z in the intervals $(y, y + dy)$ and $(z, z + dz)$. In this way we find

$$p(x)dx = p(y)dy + p(z)dz \tag{3.68}$$

Introducing now

$$x = f(y), \qquad x = f(z) \tag{3.69}$$

and

$$dx/dy = f'(y), \qquad dx/dz = f'(z) \tag{3.70}$$

we get the functional relation

$$p(x) = \frac{p(y)}{f'(y)} + \frac{p(z)}{f'(z)} \tag{3.71}$$

We call this the (stationary) Perron-Frobenius equation. In the general case the analytic solution of the Perron-Frobenius relation is not known. However a solvable case is just the logistic map with $r = 4$ and

$$y = \frac{1}{2} - \frac{1}{2}\sqrt{1-x}, \qquad z = \frac{1}{2} + \frac{1}{2}\sqrt{1-x}. \tag{3.72}$$

$$|f'(y)| = |f'(z)| = 4\sqrt{1-x}$$

In this case the Perron-Frobenius equation assumes the form

$$p(x) = \frac{p(\frac{1}{2} - \frac{1}{2}\sqrt{1-x})}{4\sqrt{1-x}} + \frac{p(\frac{1}{2} + \frac{1}{2}\sqrt{1-x})}{4\sqrt{1-x}} \tag{3.73}$$

On can check that the normalized solution is given by

$$p(x) = \frac{1}{\pi\sqrt{x(1-x)}} \qquad if \qquad 0 \le x \le 1. \tag{3.74}$$

This probability distribution has integrable poles at $x = 0$ and $x = 1$ and a minimum at $x = 0.5$. For the tent map the Perron-Frobenius equation reads

$$p(x) = \frac{1}{r}\left[p(\frac{x}{r}) + p(1 - \frac{x}{r})\right] \tag{3.75}$$

This equation is solved analytically for $r = 2$ by the homogeneous distribution

$$p(x) = 1 \qquad if \qquad 0 \le x \le 1. \tag{3.76}$$

In the general case $p(x)$ cannot be found analytically however there is no problem in finding it by numerical procedures.

For example we can solve eq.(3.71) by successive iterations starting from certain guess, e.g. the equal distribution which we introduce at the right hand side, calculate the left side etc.. Following a theorem of Lasota and Yorke, $p(x)$ is continuous if $f(x)$ is everywhere expanding. In other cases $p(x)$ might be the sum of a continuous function and Dirac δ-functions. Having obtained the probability distribution we get the Shannon entropy of the distribution by integration

$$H = \int dx p(x) \cdot \ln(1/p(x))$$

This gives in the case of the logistic map at $r = 4$ the entropy

$$H = \ln(\frac{\pi}{4}). \tag{3.77}$$

Further we obtain for the tent map at $r = 2$ the entropy

$$H = 0 \tag{3.78}$$

The probability distributions given above are is the stationary (invariant) distribution. They correspond to the invariant probability measures introduced in section 3.2 in connection with the term ergodicity. We may also discuss the time evolution for the distribution $p(x)$ which is described by the time-dependent Perron-Frobenius equation. In conclusion we undeline the remarkable result, that a purely deterministic, but chaotic dynamics, may define a smooth probability distribution.

3.4 Hamiltonian dynamics: The Liouville equation

As a first elementary example we consider a mechanical system with the linear Hamiltonian (p, q are the action and the angle)

$$H = \beta p - \alpha q. \tag{3.79}$$

We assume periodic boundary conditions on the surface of the two-dimensional unit square $0 < q < 1, 0 < p < 1$. The equations of motion are given by

$$\dot{p} = \alpha; \qquad \dot{q} = \beta \tag{3.80}$$

The solutions are are easily given

$$p(t) = p(0) + \alpha t; \qquad q(t) = q(0) + \beta t. \tag{3.81}$$

By eliminating the time we see that the phase trajectory is given on the unit square by

$$p(t) = p(0) + \frac{\alpha}{\beta}(q(t) - q(0)) \tag{3.82}$$

If (α/β) is a rational number,

$$(\alpha/\beta) = m/n, \tag{3.83}$$

then the trajectory will be periodic and will repeat itself after a period. If α/β is irrational, then the trajectory will be dense in the unit square (but will not necessarily fill it completely). One can show that our system is ergodic, i.e. for any phase function $F(q, p)$ the relation

$$< F(q, p) >_t = < F(q, p) >_s = \int dq dp F(q, p) \tag{3.84}$$

holds. In other words, the time average is equal to an ensemble average and there exists an invariant density which is $\rho = 1$. The proof of eq.(3.84) is simple (Reichl, 1987). This simple example shows, that there exist Hamiltonian systems which observe the general formalism, which requires the existence of probability densities.

Let us consider now the classical mechanics of systems with a more realistic Hamiltonian. We will assume that the Hamiltonian is defined on a space of f coordinates $q = q_1, ..., q_f$ and f momenta $p = p_1, ..., p_f$. For a large class of systems the Hamiltonian is the sum of a momentum-dependent kinetic energy and a coordinate-dependent potential energy

$$H(q_1, ..., q_f, p_1, ..., p_f) = T(p_1, ..., p_f) + U(q_1, ..., q_f) \qquad (3.85)$$

By integration of the Hamiltonian equations (3.34) at given initial state $q_i(t)$, $p_i(t)$, $(i = 1, ..., f)$ we may calculate the future state at $t + \delta t$ in a unique way. One of the most important results of modern physics is, that in spite of the deterministic connection between initial and future states, limited predictability occurs. This is due to the fact that most complex Hamiltonian systems are chaotic. However before we discuss this question in more details, let us first look at the simpler question of the reversibility of mechanical motion. Mechanical motions as e.g. the orbits of planets may go in both directions. Forward and backward movement are both allowed, the motion is reversible. On the other hand, macroscopic motions, as one of a comet falling down to earth are irreversible, they cannot go in backward direction. The reversibility of the mechanical motion is formally due to the invariance of the Hamilton equations with respect to the so-called T-transformation, which models the reversal of motion. Let us assume now that $q(t)$ and $p(t)$ are solutions of the Hamilton equations. The T-transformation leading to reversal of motion at time $t = 0$ is given by $(i = 1, 2, ..., f)$

$$q_i(t) \rightarrow q_i'(t) = q_i(-t)$$

$$p_i(t) \rightarrow p_i'(t) = -p_i(-t) \qquad (3.86)$$

One can show easily, that the $p_i'(t)$ and the $q_i'(t)$ are solutions of the Hamilton equation, i.e. they correspond to allowed motions. A similar argument is true for the quantum-mechanical motion, where the T-transformation is given by

$$\psi(q_1, ...q_f, t) \rightarrow \psi'(q_1, ..., q_f, t) = \psi^*(q_1, ..., q_f, -t). \qquad (3.87)$$

Here ψ is the wave function and ψ^* its complex conjugate. The wave function should satisfy the Schrödinger equation

$$\partial_t \psi(q_1, ..., q_f, t) = \mathbf{H} \psi(q_1, ..., q_f, t) \qquad (3.88)$$

where $\mathbf{H}$ is the Hamilton-operator. One can easily show now, that ψ' is also a solution of the Schrödinger equation, i.e. it represents a possible motion of the system. Since the times of Boltzmann, Loschmidt, Poincare and Zermelo there is a never ending discussion about the origin of the breaking of time symmetry observed in macroscopic physics (see e.g. Linde, 1984; Prigogine & Stengers, 1988; Prigogine, 1989; Ebeling, et al., 1990). Our point of view is in brief, that the observed irreversibility might be a property of the expanding world in which we are living. The second law is a basic property of this, our actual Universe. A priori we cannot exclude the possibility that in contracting phases of the Universe or in other Universes (if such

exist) the second law is not valid. Actually all our observations refer to the expanding Universe surrounding us . Merely for philosophical reasons we share Boltzmann's and Einstein's view, that globally the world is uniform in space and time. Stationarity on big scales is one of its basic properties. Boltzmann expressed his views in the following sentences (quotation from Brush, 1965): *"The second law of thermodynamics can be proved from the mechanical theory if one assumes, that the present state of the universe, or at least that part that surrounds us, started to evolve from an improbable state and is still in a relatively improbable state. This is a reasonable assumption to make, since it enables us to the facts of experience, and one should not expect to be able to deduce it from anything more fundamental. ... . For the universe as a whole, there is no distinction between the "backwards" and "forwards" directions of time, but for the worlds on which living beings exist, and which are therefore in relatively improbable states, the direction of time will be determined by the direction of increasing entropy, proceeding from less to more probable states"*. We believe, that Boltzmann, who was a really deep thinker, was right in the general respect, his views were just limited by the knowledge of his time. Nowadays our knowledge about the fundamental laws of dynamics is no more limited to the classical mechanics. Modern physics is based on quantum mechanics, general relativity theory on the big scales and quantum field theories on the small scales. Let us imagine how Boltzmann would rephrase his ideas in our days, nearly 100 years after his reply to Zermelo's paper. Probably Boltzmann would start from general relativity, quantum field theories, relativistic thermodynamics and modern cosmological theory (Neugebauer, 1980; Linde, 1984). Guided by his general view about stationarity he would like the model of the closed Universe which has oscillating solutions (Linde, 1984). Modifying the standard picture about regular oscillations, Boltzmann would possibly assume stochastic oscillations. He would not insist on the purely thermal character of the oscillations but would admit as well vacuum fluctuations. Maybe he would say that our Universe is subject to some colored noise with a basic period of about 1 - 100 billions of years. Still he would insist on his hypothesis: *"Among these worlds the state probability increases as often as it decreases. For the Universe as a whole the two directions of time are indistinguishable, just as in space there is no up or down"*. We believe that the laws of macroscopic physics are deeply affected by the expansion of our Universe. Expanding space soaks up radiation and acts as a huge thermodynamic sink for all radiation. At present the whole Metagalaxis is filled with a sea of thermal photons having a density of about $500 cm^{-3}$ and a temperature of about 2.7 K. This so-called background radiation acts as a thermal heat bath which influences all motions of particles in an irreversible way.

Following Boltzmann's view that our world is basically probabilistic, let us consider now the question, how probabilities may be introduced into a many-particle classical mechanical system and what is the dynamics of these probabilities. We postulate that the system may be characterized at time t by a probability density

$$\rho(q_1, ...q_f, p_1, ..., p_f, t) \tag{3.89}$$

such that the ensemble average (3.56) of any given phase function F is defined. Trying to find

an equation which determines the time evolution of the probability density we note first, that the reversibility of the mechanical motion requires

$$\frac{d\rho}{dt} = 0. \tag{3.90}$$

Here d/dt denotes the substantial derivation corresponding to a coordinate system moving with the phase point. An observer moving on the flow in the phase space will see a constant probability, otherwise he could differ between the past and the future. The so-called Liouville equation (3.90) is equivalent to the well-known invariance of the phase volume with respect to motion. Let us transform now eq. (3.90) by using the Hamilton equations (3.34). We get

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_r \left(\frac{\partial\rho}{\partial q_r}\dot{q}_r + \frac{\partial\rho}{\partial p_r}\dot{p}_r\right) = 0 \tag{3.91}$$

This is the explicite form of the Liouville equation which we may write formally, employing the Poisson brackets, as

$$\frac{\partial\rho}{\partial t} + [H, \rho] = 0 \tag{3.92}$$

There exists a different way to derive the Liouville equation starting from the property of the Hamiltonian flow to be free of sources (see Chapter 2). This way we get

$$\frac{\partial\rho}{\partial t} + \sum_r \left(\frac{\partial\rho\dot{q}_r}{\partial q_r} + \frac{\partial\rho\dot{p}_r}{\partial p_r}\right) = 0. \tag{3.93}$$

By using the fact that the divergence of Hamilton flows is zero

$$\rho\sum_r \left(\frac{\partial\dot{q}_r}{\partial q_r} + \frac{\partial\dot{p}_r}{\partial p_r}\right) = 0. \tag{3.94}$$

we arrive again at the Liouville equation eq.(3.92).

The Liouville equation is still reversible; strictly speaking it is not a kinetic equation. We may compare it with the Frobenius-Perron equation introduced in section 3.3. Stationary solutions of eq.(3.92) are easily found. We have to observe however several requirements, a probability has to fulfill, as smoothness and integrability.

A rather general solution is

$$\rho(q_1, ...q_f, p_1, ..., p_f) = F\left(H(q_1, ...q_f, p_1, ..., p_f)\right) \tag{3.95}$$

with a free function F which is arbitrary up to certain requirements. One example of a stationary solution of this type is

$$\rho(q_1, .., q_f, p_1, .., p_f) = C\exp[-\beta H(q_1, ..q_f, p_1, .., p_f)] \tag{3.96}$$

where C and β are positive constants. Later this distribution will get the name "canonical". Further any function of constants of motion is a stationary solution. Namely, in the case we can find s constants of the motion $I_1, .., I_s$ which are single valued differential (analytic) functions. Furthermore these s functions must be independent of each other and exist globally, i.e. for all allowed values of the coordinates and momenta. Then, again for a rather general class of functions F we find a whole class of solutions in the form

$$\rho(q_1, ..., q_f, p_1, ..., p_f) = F(I_1, .., I_s) \tag{3.97}$$

The problem with the Liouville equation is, that it has so many solutions. In this way we come back to Boltzmann's hypothesis stating that possibly the Hamiltonian is the only single valued analytic integral of motion, i.e. the solutions of type (3.96) expressing Gibbs' canonical distributions would be sufficiently general.

Why should this be true? The key ideas are based on Poincare's work from 1890, about the instability of many-body motions. The further development of this work we owe especially to Birkhoff, Hopf, Krylov, Born, Kolmogorov, Arnold, Moser, Sinai, Chirikov, Zaslavskii and others. We have explained the concept of instability and Lyapunov exponents already in the previous chapter. Let us repeat the main ideas in brief: The states and the trajectories of dynamical systems are never exactly known and are subject to stochastic perturbations. Therefore the stability of motion with respect to small changes is of large interest. The stability of trajectories $\boldsymbol{x}(t) = [q_1(t), ..., q_f(t), p_1(t), ..., p_f(t)]$ is studied by investigating besides the original trajectories $\boldsymbol{x}(t; \boldsymbol{x}_0, t)$ which starts at $\boldsymbol{x}_0, t_0$ also a second one $\boldsymbol{x}(t; \boldsymbol{x}_0 + \delta\boldsymbol{x}_0, t_0)$, which at the initial time t_0 starts at $\boldsymbol{x}_0 + \delta\boldsymbol{x}_0$ where $\delta\boldsymbol{x}_0$ is a small shift vector. The motion is called globally stable if for all t and any $\epsilon > 0$ there exists always an $\eta(\epsilon, t_0)$ such that for $|\delta\boldsymbol{x}(t_0)| < \eta$ follows $|\delta\boldsymbol{x}(t)| < \epsilon$ for any $t > t_0$. If such an η does not exist, the motion is called unstable.

From a more detailed analysis of the instability we obtain the spectrum of eigenvalues of singular points, the spectrum of Floquet exponents of periodic orbits and the spectrum of Lyapunov exponents. These exponents are all related to the properties of the Jacobian $\boldsymbol{J}$ defined earlier by eq.(2.89) of the dynamical system.

For Hamilton systems the trace of the Jacobian is zero

$$Tr\boldsymbol{J}(\boldsymbol{x}) = 0. \tag{3.98}$$

Correspondingly the eigenvalues are either real, consisting of symmetrically located pairs or conjugated imaginary. This means that we will not find asymptotically stable singular points. All singular points will be of saddle type or centers. An analog statement can be given for the stability of periodic orbits. The sum of the Lyapunov-exponents λ_i is always zero

$$\sum_i \lambda_i = 0 \tag{3.99}$$

what corresponds to the conservative character of Hamiltonian systems. If at least one (the largest) Lyapunov exponent is positive, the motion is chaotic. Generally we expect that the

real parts of the spectrum have positive and negative contributions

$$\lambda_1 \geq ... \geq \lambda_j > 0 > \lambda_{j+1} \geq ... \geq \lambda_n \tag{3.100}$$

Then the sum of the positive Lyapunov exponents is in most cases equal to the Kolmogorov entropy (Pesin, 1977 ; Ledrappier & Young, 1985). The Kolmogorov entropy is closely connected with the problem of the predictability of motions (Eckmann & Ruelle, 1985). Originally Kolmogorov introduced this quantity on the basis of the many-point entropies of the Shannon theory (Kolmogorov, 1958). Here we use only the simplified version based on the λ-spectrum. Let us define the Pesin - entropy by (Pesin, 1977; Ebeling, Steuer & Titchener, 2001)

$$K_\lambda = \sum_i^+ \lambda_i, \qquad (\lambda_i > 0). \tag{3.101}$$

The Pesin entropy is identical to the Kolmogorov entropy for a big class of interesting systems (Pesin identity) (Pesin, 1977, Eckmann & Ruelle, 1985). The dynamics is characterized as unstable if $K_\lambda > 0$. If $K_\lambda > 0$ for a certain region of the phase space we say that this region is stochastic. In this case predictability is quite limited. Trajectories tend to diverge at least in certain directions, what makes long term predictions impossible. Small uncertainties at zero time will arrive at very large values very soon.

One of the most important results of the modern theory of Hamiltonian systems is, that most many-body systems have stochastic regions (Krylov, 1950, 1979; Arnold and Avez, 1968; Sinai, 1970, 1972; Chirikov, 1979; Lichtenberg and Lieberman, 1983; Zaslavskij, 1984; Arnold, 1987). Systems with positive K - entropy are called now K-systems or K - flows. The property of being a K-flow includes mixing and ergodicity. The opposite however is not true. Sinai (1970, 1972) has shown that systems of $N > 2$ hard spheres in a box with hard walls are K-systems. This makes rather probable that all systems of particles with rather hard repulsion are also K-systems. We consider this to be one of the most important results of modern statistical mechanics.

3.5   Markov models

In the previous two sections we have considered several examples of chaotic dynamical systems leading to stationary probability densities, corresponding to invariant measures (Lasota & Mackey, 1985). For a simple example we shall demonstrate now, how Markov models for the dynamics may be derived. Such Markov models correspond to irreversible kinetic equations for the process to be described. Following the work of Nicolis, Piasecki and Mc Kernan (1992) we study first the tent map (3.59) (Nicolis, Martinez & Tirapegui, 1991; Nicolis, Piasecki and Mc Kernan, 1992; Mc Kernan, 1993; Nicolis and Gaspard, 1993)

$$x(t+1) = rx(t) \qquad if \qquad x \leq 0.5$$

$$x(t+1) = r[1 - x(t)] \qquad if \qquad x > 0.5. \tag{3.102}$$

The time-dependent version of the Perron-Frobenius equation for the tent map is obtained by a generalization of eq.(3.66). Considering the balance of probabilities at time t and $t + 1$ we obtain

$$p(x, t+1) = \frac{1}{r} \left(p(\frac{x}{r}, t) + p(1 - \frac{x}{r}, t) \right) \tag{3.103}$$

Let us consider now the special parameter value $r = 2$; then the map is fully chaotic and the time evolution is given by:

$$p(x, t+1) = \frac{1}{2} \left(p(\frac{x}{2}, t) + p(1 - \frac{x}{2}, t) \right) \tag{3.104}$$

As we can verify by substitution, the stationary distribution is given by

$$p_0(x) = 1 \qquad if \qquad 0 < x < 1. \tag{3.105}$$

In other words, the equal distribution satisfies the stationary Perron-Frobenius equation at $r = 2$. The mean uncertainty corresponding to the equal distribution (3.105) is $H = 0$. Any other normalized distribution has a lower value of the mean uncertainty. This is exactly the behavior we expect from the point of view of thermodynamics. We note, that for continuous distributions the mean uncertainty is not always positive definite. Another more serious problem with the Perron-Frobenius equation (3.103) is, that an initial distribution must not necessarily converge to the stationary distribution. In other words, we have no irreversibility of the evolution, no Markov property. The solution of this problem comes from the rather old idea of coarse-graining introduced already by Gibbs. The introduction coarse-grained descriptions leads us and to evolution equations with Markov character. So far we have considered a fine (microscopic) description of our dynamic system based on the exact state $x(t)$ at any time t or the corresponding distribution $p(x, t)$. A coarse description does not specify the state exactly but only with respect to certain intervals. Let us introduce a partition of the state space by

$$\boldsymbol{P} : [C_1, ..., C_\lambda], \qquad C_i \cup C_j = 0 \qquad \text{if} \qquad i \neq j \tag{3.106}$$

$\boldsymbol{P}$ is called a partition of the interval $[0, 1]$. Now we restrict our description by giving only the number of the interval in which the exact state $x(t)$ is located. On this coarse-grained level the state is one of the λ discrete possibilities. The corresponding dynamics is a hopping process between the intervals. Since the hopping is a discrete process, the description of the dynamics has necessarily to use stochastic methods. We note at this place that for for discrete processes deterministic descriptions do not exist. This is an important point. For the case of continuous state spaces we have a free choice between deterministic and probabilistic descriptions, both are strictly equivalent. After introducing coarse-graining no deterministic description exists anymore and the stochastic description is a must. Let us introduce $P(i, t)$ as the probability of

finding the system at the time t on the level (the interval) i. In exact term this probability is defined by

$$P(i,t) = \int_{C_i} dx \cdot p(x,t) \tag{3.107}$$

In accordance with our general reasoning we assume now that the evolution of the probability is a Markov process defined by a stochastic matrix $\boldsymbol{W} = [W_{ij}]$ and the equations

$$P(i, t+1) = \sum_j W_{ij} P(j,t) \tag{3.108}$$

with

$$\sum_i W_{ij} = 1$$

The problem with the rough descriptions is, that the Markov picture might not exist or be incompatible with eqs.(3.106-3.108). In any case a general proof of the existence of Markov descriptions seems to be difficult. A partition of the original phase space which leads to a Markov description is called a *Markov partition*. Evidently no general prescription is known, how to find Markov partitions for an arbitrary given dynamics. However several rules are known, which might be helpful in finding Markov partitions for given deterministic dynamics. An example where this procedure works was demonstrated by Nicolis et al. (1991,1992). We will discuss this example here without giving a full prove. Let us now consider again the tent map with $r = 0.5(1 + \sqrt{5})$. For this map the dynamics is chaotic and has an attractor located in the interval $[r(1-r/2), r/2]$. This means, in the coarse of the time evolution, any initial state will be attracted by this interval. In the coarse grained description a 2-partition is generated by means of the maximum of the tent at 0.5:

$$C_1 = [0, 0.5), \qquad C_2 = [0.5, 1] \tag{3.109}$$

The resulting states, denoted e.g. by "L" and "R"" may be viewed as the letters of an alphabet. Then following Nicolis et al. (1992) the stochastic matrix $\boldsymbol{W}$ is exactly given by

$$W_{11} = 0 \qquad W_{12} = 1/r^2 \tag{3.110}$$
$$W_{21} = 1 \qquad W_{22} = 1/r \tag{3.111}$$

We can easily verify the Markov properties

$$W_{11} + W_{21} = 1, \qquad W_{12} + W_{22} = 1.$$

Further we verify, that the stationary (invariant) distribution has the components

$$P(1) = 1/(1+r) = 0.27639....$$

$$P(2) = r/(1+r) = 0.72360... \tag{3.112}$$

A direct proof of these relations may be given by comparison by carrying out the integrations in eq.(3.108), this way we may confirm that eq.(3.111) and eq.(3.112) are true. Some generalization of this description is possible for the 4-partition

$$C_1 = [r(1 - r/2), 1/2]; \qquad C_2 = [1/2, r/2]; \tag{3.113}$$
$$C_3 = [0, r(1 - r/2)]; \qquad C_4 = [r/2, 1] \tag{3.114}$$

After some transitory dynamics, the attractor is reached, which cannot be left, i.e. the transitions $1 \to 3$, $1 \to 4$, $2 \to 3$, $2 \to 4$ are impossible. The corresponding matrix elements should disappear.

$$W_{13} = 0 \qquad W_{14} = 0 \qquad W_{23} = 0 \qquad W_{24} = 0$$

The matrix elements $W_{11}, W_{21}, W_{12}, W_{22}$ remain unchanged. The message is, that there might be several Markov descriptions for a given deterministic dynamics.

Another example which can be treated this way is the logistic map at $r = 4$, where also a family of Markov partitions is known. For instance, the points of the unstable periodic orbits $x = 0.345...$; $x = 0.905...$ define a three-cell Markov partition. The resulting 3 states, e.g. "O", "L" and "M" by be considered again as an alphabet. As shown by Nicolis et al. (1989) the corresponding probability matrix has the elements

$$W_{11} = 1/2 \qquad W_{12} = 0 \qquad W_{13} = 1 \tag{3.115}$$
$$W_{21} = 1/2 \qquad W_{22} = 1/2 \qquad W_{23} = 0 \tag{3.116}$$
$$W_{31} = 0 \qquad W_{32} = 1/2 \qquad W_{33} = 0. \tag{3.117}$$

Many other examples for generating Markov partitions are known. However the deep problem remains open, what are in general the conditions for making a transition to Markov descriptions. Evidently Markov-like descriptions are the condition sine qua non for the formulation of a "statistical mechanics" including "kinetic equations" and the irreversible transition to an "equilibrium thermodynamics". In conclusion we may state that nonlinear systems in the chaotic regime are leading to probabilistic and thermodynamic descriptions in a quite natural way. In other words, nonlinearity, chaos, and thermodynamics are closely linked together. This point will occur to be fundamental for all the problems discussed in this book. This was the reason to explain this connection for simple examples already at the beginning of this book.

Our basic hypothesis is, even without having a general prove of this statement, that the macroscopic systems which are the objects of "statistical physics" have similar properties as the simple chaotic maps studied in this Chapter.

Chapter 4

Entropy and Equilibrium Distributions

4.1 The Boltzmann-Planck principle

According to our general concepts, Statistical Physics is the bridge between the microscopic and macroscopic levels of description. Basic tools are probability and entropy. We have shown in the last Chapter how these concepts come into play. Probability may be introduced axiomatically as we did in Chapter 2 as an appropriate concept for the description of mesoscopic or macroscopic systems. However, and this is even more interesting in the present context, it may arise (see sections 3.3 - 3.5) in a natural way if the dynamics of systems is chaotic. Having probabilities we may calculate entropies as first done for physical systems by Boltzmann (see section 3.1). Entropy concepts were used already several times in the previous Chapters. In the introduction we gave, based on the historical point of view, a brief discussion of the probabilistic physical entropy concept developed in the pioneering work of Boltzmann, Planck and Gibbs. As we mentioned already, strictly speaking this concept has still an earlier root in game theory. Already in the 18th century DeMoivre used the expression $\log(1/p_i)$ as a measure for the uncertainty of predictions in the context of describing the outcome of games. The mathematical concept, *entropy as mean uncertainty*, was worked out later by Shannon, who formed the basis of the modern information theory. Shannon's information theory has nowadays very many applications reaching from technology, to medicine and economy. The concept of entropy used in the stochastic theory is also based on Shannon's entropy.

In order to explain these ideas in brief, we consider a system with discrete states numbered with $i = 1, , s$ which are associated with the probabilities p_i. The states i are standing here for certain states of order parameters of the system. Then the Shannon entropy is defined as the mean uncertainty per state

$$\mathcal{H} = \langle \log(1/p_i) \rangle = -\sum_i p_i \log p_i. \tag{4.1}$$

This quantity is always between zero and one:

$$0 \leq \mathcal{H} \leq 1 \tag{4.2}$$

The mean uncertainty is zero, if all the probability is concentrated on just one state

$$\mathcal{H} = 0 \qquad if \qquad p_k = 1, \qquad p_i = 0 if \qquad i \neq k \tag{4.3}$$

On the other hand the uncertainty is maximal, if the probability is equally distributed on the states

$$\mathcal{H} = 1 \qquad if \qquad p_i = 1/s \qquad i = 1, ..., s \tag{4.4}$$

The equal distribution corresponds to maximal uncertainty. This property will play an important role in the considerations in the last section of this Chapter. Another important fact is that $\mathcal{H}$ has the property of additivity. In order to prove this we consider two weakly coupled systems 1 and 2 with the states i and j respectively and with

$$p_{ij}^{12} = p_i^1 \cdot p_j^2 \tag{4.5}$$

Using this relation we can show quickly that the mean uncertainty is an additive function

$$\mathcal{H}^{12} = \mathcal{H}^1 + \mathcal{H}^2 \tag{4.6}$$

This way, the mean uncertainty has quite similar properties as the entropy and we arrive at the hypothesis that both quantities are closely related, may be even proportional. Still we have to find out, what are the conditions for a proportionality.

The expression for the mean uncertainty may be generalized to continuous state spaces. Let us assume that x is a set of n order parameters on the dynamic-stochastic level of description. If $p(x)$ denotes the probability density for this set of order parameters which describe the macroscopic state, the mean uncertainty (informational entropy) of the distribution (the $\mathcal{H}$ - function) is defined by

$$\mathcal{H} = -const \int dx \; p(x) \cdot \log p(x) \tag{4.7}$$

In the case of discrete variables $i = 1, 2, , s$ we come back to the classical Shannon expression with a sum instead of the integral. As well known these are the basic formulas of information theory. We shall come back to this later several times.
In order to come from the general expression for the mean uncertainty (informational entropy) to Boltzmann's physical entropy we identify the state space with the phase space of one molecule $\boldsymbol{q}, \boldsymbol{p}$: Then the Boltzmann's mean uncertainty of states in phase space is given by

$$H_B = -\int \frac{d\boldsymbol{p} d\boldsymbol{q}}{h^3} f(\boldsymbol{p}, \boldsymbol{q}, t) \cdot \ln f(\boldsymbol{p}, \boldsymbol{q}, t), \tag{4.8}$$

Here $f(\boldsymbol{p}, \boldsymbol{q}, t)$ is the one-particle distribution function. Further we introduced a constant h with the dimension of an action. This was h^3 has the same dimension as $d\boldsymbol{p} d\boldsymbol{q}$ and this makes the whole integral dimensionless. Here is a point where classical theory has to borrow results from quantum theory. Heisenberg's uncertainty relation teaches us, that there is no way to

measure location and momentum at the same time with an accuracy better than h (Planck's constant). This makes h^3 the natural choice for the minimal cell in Boltzmann's theory. We compare now our results with the Boltzmann formula for the entropy of ideal gases. As shown in the previous chapter, the Boltzmann entropy of ideal gases is given by

$$S_B = -k_B \int \frac{d\boldsymbol{p}d\boldsymbol{q}}{h^3} f(\boldsymbol{p},\boldsymbol{q},t) \cdot \ln f(\boldsymbol{p},\boldsymbol{q},t), \qquad (4.9)$$

with the normalization

$$N = \int \frac{d\boldsymbol{p}d\boldsymbol{q}}{h^3} f(\boldsymbol{p},\boldsymbol{q},t). \qquad (4.10)$$

We see that Boltzmann's entropy is proportional to the uncertainty of molecular states:

$$S_B = k_B H_B \qquad (4.11)$$

where k_B is the universal Boltzmann constant.

For the generalization to interacting systems we must realize in accordance with Chapter 3, that the new state space is the phase space of all the N molecules in the system. For this general case we introduce after Gibbs the normalized probability density ρ in the $6N$-dimensional phase space. Assuming that Shannon's state space is the phase space of all the molecules forming the system, the Shannon entropy of the system is given by the N-particle probability ρ. Therefore Gibbs' mean uncertainty H_G is the phase space entropy for the distribution of the molecules in the total phase space

$$H_G = -\int \frac{d\boldsymbol{p}^N d\boldsymbol{q}^N}{h^{3N}} \rho(\boldsymbol{q}^N,\boldsymbol{p}^N) \cdot \ln \rho(\boldsymbol{q}^N,\boldsymbol{p}^N). \qquad (4.12)$$

By multiplication with Boltzmann's constant we get the statistical Gibbs entropy

$$S_G = k_B H_G \qquad (4.13)$$

or explicitly

$$S_G = -k_B \int \frac{d\boldsymbol{p}d\boldsymbol{q}}{h^{3N}} \rho(\boldsymbol{q}^N,\boldsymbol{p}^N) \cdot \ln \rho(\boldsymbol{q}^N,\boldsymbol{p}^N) \qquad (4.14)$$

Now the basic theorems of statistical thermodynamics tell us, that in the case of ideal gases the Boltzmann entropy equals the thermodynamic entropy, i.e.

$$S_B = S. \qquad (4.15)$$

For interacting systems we postulate that the thermodynamic entropy corresponds to the Gibbs entropy

$$S_G = S. \qquad (4.16)$$

In this way - in some sense - the thermodynamic entropy may be considered in a specific (formal) sense as a special case of the Shannon entropy. It is (up to a constant) just the mean uncertainty of the location of the molecules in the phase space. The close relation between the thermodynamic entropy and the Shannon entropy is the solid basis for the embedding of the information concept into the theoretical physics (Brillouin, 1956; Grandy & Schick, 1991).

The Gibbs expression includes all interaction effects which in general lead to a decrease of the value of the entropy in comparison to the ideal gas (Ebeling & Klimontovich, 1984). In principle, eq.(4.11) works for nonequilibrium states as well, however this is true only *cum grano salis* as we will see later. In a different but closely related approach developed by Boltzmann and Planck the entropy of a macrostate was defined as the logarithm of the thermodynamic probability

$$S_{BP} = k_B \ln W. \tag{4.17}$$

which is defined as the total number of equal probable microstates corresponding to the given macro state. This fundamental formula is carved on Boltzmann's gravestone in the *"Zentralfriedhof"* cemetery in Vienna.

For the special case of equilibrium systems with fixed energy E the Gibbs relations eqs. (4.11) and (4.13) reduce to the Boltzmann-Planck formula (4.14).

Let us mention further on that after Einstein one may invert relation (4.14) what gives us the probability that the nonequilibrium state occurs as the result of a spontaneous fluctuation

$$W(y_1, y_2, ..., y_n) = const \exp[-\delta S(y_1, y_2, ..., y_n)/k_B] \tag{4.18}$$

where δS is the lowering of entropy. We will come back to this relation in Chapter 5 and use it as a basis for developing Einstein's theory of fluctuations.

Another interesting aspect aspect of eq. (4.15) is its relation to considerations on measures of distance from equilibrium (see Chapter 2). The inspection of relation (4.15) shows directly that δS is a kind of measure of the distance from equilibrium (at $E = const$) since equilibrium is the most probable state .

In Shannon's approach the basic role play some order parameters x and the corresponding probabilities $p(x)$ or p_i. In order to find a closer connection to the Boltzmann-Gibbs approach, we have to consider the order parameters as certain functions of the microscopic variables.

$$x = x(q_1, ..., p_{3N}) \tag{4.19}$$

Let us assume now that Gibbs' probability density may be represented as the product of the probability density in the order parameter space and the conditional probability (formula of Bayes)

$$\rho(p, q) = \int p(x) \cdot \rho(p, q|x) dx \tag{4.20}$$

Then a brief calculation yields

$$S_G = k_B H + S_b \tag{4.21}$$

with

$$S_b = \int p(x)S(x)dx \tag{4.22}$$

$$S(x) = -k_B \int \frac{d\boldsymbol{p}d\boldsymbol{q}}{h^3} \rho(p,q|x) \log \rho(p,q|x) \tag{4.23}$$

Here $S(x)$ is the conditional statistical entropy for a given value of the order parameter x. In this way we have shown that, up to a factor, the Shannon entropy of an order parameter is a fully legitimate part of the Gibbs entropy. As eq.(4.21) shows, the contribution $k_B H$ constitutes the statistical entropy contained in the order parameter distribution. In general this is a very small part of the total statistical entropy, the overwhelming part comes from the term S_b. The part collected in S_B reflects the entropy contained in the microscopic state, it is not available as information. Let us give an example: The Gibbs entropy of a switch with two states is the sum

$$S_G = k_B \log 2 + S_b \tag{4.24}$$

where S_b is the usual (bound) entropy in one of the two positions. The two contributions to the total entropy are interchangeable in the sense discussed already by Szilard, Brillouin and many other workers (Denbigh & Denbigh, 1985). Information (i.e. macroscopic order parameter entropy) may be changed into thermodynamic entropy (i.e. entropy bound in microscopic motions). The second law is valid only for the sum of both parts, the order parameter entropy and the microscopic entropy.

4.2 Isolated systems: The microcanonical distribution

From the point of view of statistical physics, as we have shown already in section 4.1, entropy is deeply connected with the mean uncertainty of the microscopic state in the phase space. Let us study now in more detail systems which are energetically isolated from the surrounding in the sense that the energy is closely concentrated around a given value E:

$$E - (1/2)\delta E \leq H \leq E + (1/2)\delta E \tag{4.25}$$

The part of the phase space enclosed by this relation is called the energy shell. In isolated systems the available part of the phase space is the volume $\Omega(E)$ of this energy shell enclosing the energy surface $H(\boldsymbol{q}, \boldsymbol{p}) = E$. Boltzmann's postulate is, that under conditions equilibrium, any point on the energy shell (more precise the neighborhood of the point) is visited equally frequent. This so-called ergodic hypothesis is physically plausible but very difficult to prove for concrete systems (Sinai, 1970, 1972, 1977). Equivalent is the assumption that the probability is constant on the shell

$$\rho(q,p) = \frac{1}{\Omega(E)} \tag{4.26}$$

Equal probability on the shell is equivalent to maximum of the entropy. Therefore thermodynamic equilibrium corresponds to maximal entropy. This property which appears here as a

consequence of certain aspects of the dynamics on the shell (ergodicity) will be turned in the last section to a first principle of statistical physics.

If the system is isolated (i.e. located on an energy shell) but not in equilibrium only certain part of the energy shell will be available. In the course of relaxation to equilibrium the probability is spreading over the whole energy shell filling it finally with constant density. Equilibrium means equal probability, and as we have seen and shall explain in more detail later, least information about the state on the shell.

We shall come back now to our basic question about the meaning of entropy. Usually entropy is considered as a measure of disorder, but the entropy is like the face of Janus, it allows other interpretations. The standard one is based on the study of phase space occupation. The number of states with equal probability corresponds to the volume of the available phase space $\Omega(A)$. Therefore the entropy is given by

$$S = k_B \ln \Omega^*(A) \tag{4.27}$$

Here A is the set of all macroscopic conditions $\Omega(A)$ the corresponding phase space and

$$\Omega^*(A) = \frac{\Omega(A)}{h^{3N} N!} \tag{4.28}$$

Here the mysterious factor $N!$ was introduced as a consequence of the indisguishability of the microscopic particles. In the nonequilibrium states the energy shell is not filled with equal density, but shows regions with increased density (attractor regions). Let $S(E,t)$ be the entropy at time t. Then we may define an effective volume of the occupied part of the energy shell by

$$S(E,t) = k \ln \Omega^*_{eff}(E,t) \tag{4.29}$$
$$\Omega^*_{eff}(E,t) = \exp[S(E,t)/k_B] \tag{4.30}$$

In this way, the relaxation on the energy shell may be interpreted as a monotonous increase of the effective occupied phase volume. This is connected with a devaluation of the energy, a point of view discussed already in section 2.3.

4.3   Gibbs distributions for closed and for open systems

Starting from the microcanonical distribution we intend now to derive the equilibrium canonical distributions for the microscopic variables of the Γ-space. First we consider the standard cases:
i) Closed systems, allowing exchange of energy with a second system.
ii) Open systems which involve additionally particle exchange.
An isolated system with energy E and volume V is divided in two subsystems, further called bath and system. Both subsystem should be macroscopic bodies and, therefore, allow the introduction of intensive thermodynamic variables. They are both in thermal equilibrium

which implies the equality of their temperatures. We label the bath volume by V_b and the volume of the system by V, respectively and evidently follows

$$V_0 = V_b + V \tag{4.31}$$

In the Hamilton function the interaction part though it is essential for the relaxation to the equilibrium state will be neglected. Therefore choosing the analogous labeling it reads

$$E_0 = H_b + H + H_{int} \simeq H_b(q_1^b, ...p_{3M}^b) + H(q_1, ..., p_{3N}) \tag{4.32}$$

Here $q_1, ...q_{3N}$ and $p_1, ..., p_{3N}$ are the microscopic variables of the system and $q_1^b, ...q_{3M}^b, p_1^b, ..., p_{3M}^b$ those of the bath, respectively. First we look for the distribution of the microscopic variables of the system if the exchange of particles is forbidden. Suppose the energy of the system is fixed at a value $H = E$. From eq.(4.32) immediately follows that the bath should possess the energy $H_b = E_b = E_0 - E$. The probability to find the microscopic variables of the considered system in states with energy E is found by collection of the probability of the bath to be in states $H = E_b$. It means

$$\rho(E) = \exp[-S_0(E_0, V_0)/k_B] \int d\Gamma_b \delta(H_b + E - E_0) \tag{4.33}$$

The integral is taken over the bath variables $q_1^b...p_{3N}^b$. Otherwise this integral gives just the thermodynamic weight of the numbers of microscopic (quantum) states of the bath which realize the volume V and the energy E_b

$$\Omega(E_b, V_b) = \int d\Gamma_b \delta(H_b + E - E_0) \tag{4.34}$$

Since the bath is considered as a macroscopic body we are able to find its thermodynamic entropy

$$S_b(E_b, V_b) = k_B \ln \Omega(E_B, V_B) \tag{4.35}$$

By inversion of this formula we are left with

$$\rho(E) = \exp[(S_b(E_0 - E, V_0 - V) - S_0(E_0, V_0))/k_B]. \tag{4.36}$$

We reformulate the expression in the exponent by using the definition of the free energy $F = E - TS$. Hence we derive

$$S_b(E_0 - E, V_0 - V) - S(E_0, V_0) = \frac{1}{T}(F_0 - F_bE) = \frac{1}{T}(F(T, V) - E) \tag{4.37}$$

where $F(T, V)$ is the free energy of the considered system. In deriving (4.37) we made use of the equality of the temperatures. Subsequently we interpret $E = H(q_1...p_{3N})$ as the Hamilton function of the microscopic variables of the system and find the canonical distribution

$$\rho(q_1, ..., p_{3N}) = \exp\left[\frac{F(T, V) - H(q_1, ..., p_{3N})}{k_BT}\right] \tag{4.38}$$

This way we derived now Gibbs' canonical distribution, already known to us from Chapter 3, from the microcanonical distribution.

The bridge between thermodynamics and statistics follows from the normalization condition of this distribution. Accordingly to

$$\int \frac{d\Gamma}{h^{3N}} \rho = 1 \tag{4.39}$$

the free energy of a system with volume V and embedded in a thermal bath with temperature T is defined by the statistical sum $Q(T, V)$

$$F(T, V) = -k_B T \ln Q(T, V) = -k_B T \ln \int \frac{d\Gamma}{h^{3N}} \exp(-\beta H) \tag{4.40}$$

The mean energy follows from the relation

$$E = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q(T, V) = k_B T \frac{\partial}{\partial T} \ln Q(T, V) \tag{4.41}$$

and the dispersion is defined by

$$\langle H^2 \rangle - (\langle H \rangle)^2 = \frac{\partial^2}{\partial \beta^2} \ln Q(T, V) = -\frac{\partial}{\partial \beta} \langle H \rangle = k_B T^2 C_V \tag{4.42}$$

This way all important thermodynamical quantities are given by the partition function $Q(T, V)$.

Quite similar we can proceed if particle exchange between the bath and the system is possible. The additional condition concerns with the conservation of the particle number of the bath and the system.

$$N_0 = N_b + N \tag{4.43}$$

The thermodynamic entropy of the bath is analogous to equation (4.37) but depends now also on N. Therefore in the exponent of the probability distribution the following difference of the entropies occurs

$$\Delta S = S_b(E_0 - E, V_0 - V, N_0 - N) - S(E_0, V_0, N_0). \tag{4.44}$$

Introducing the thermodynamic potential $\Xi = -pV$ it becomes

$$\Delta S = \frac{1}{T}(\Xi + \mu N - E) \tag{4.45}$$

and we end with

$$\rho_N(q_1, ..., p_{3N}) = \exp\left[\frac{\Xi + N\mu - H_N}{k_B T}\right] \tag{4.46}$$

By using again a normalization condition which reads now

$$1 = \sum_N \int \frac{dq_1...dp_{3N}}{N! h^{3N}} \rho_N(q_1, ..., p_{3N}) \tag{4.47}$$

we find a relation between thermodynamics and statistical quantities

$$\Xi = -kT \ln \sum_N \int \frac{d\Gamma}{N! h^{3N}} \exp[-\frac{H_N}{k_B T}] \tag{4.48}$$

In conclusion let us shortly comment on the general procedure how the canonical distributions were derived from the microcanonical one. First of all the fixed energy of the system defined by the microscopic state was interpreted as an extensive thermodynamic variable of the system, further we neglected the interaction energy. Secondly the exponents in the distributions (4.38) and (4.46) correspond to that value of the overall entropy when the temperatures of the bath and the system have been equilibrated. The overall entropy is maximized under the constraints E, V, N for the considered system and E_0, V_0, N_0 for bath plus system. Our result could be derived also from the minimal reversible work which has to be applied isoenergetically to generate the state of our system embedded in the bath.

$$\Delta S = -\frac{1}{T} R_{min}. \tag{4.49}$$

This minimal work obviously depends on the actual thermodynamic embedding of the considered system. In the case of a closed system where the volume and temperature are constant $R_{min} = F(T, V) - H$. Fixing the pressure instead of the volume we would have

$$R_{min} = G(T, p) - H = F(T, V) + pV - H. \tag{4.50}$$

with $G(T, p)$ being the Gibbs free energy.

4.4 The Gibbs-Jaynes maximum entropy principle

Summarizing and looking again at the previous derivations of Gibbs ensembles, one might be not too happy with the logical built-up of the theory. We started with the Boltzmann-Planck expression for the entropy of systems with equally probable states, applying this formula to macroscopically isolated systems with fixed energy. In fact we postulated that constant probability on the energy shell is given *a priori*. Also we did not care much about the mathematical difficulties to prove "ergodicity" for concrete systems. In a following step we derived, by using some embedding procedure, the probability distributions for other situations, as e.g. systems in a heat bath.

The great follower of Gibbs' work E.T. Jaynes criticizes this approach with the following remarks (Jaynes, 1985): *"A moment's thought makes it clear how useless for this purpose is our conventional textbook statistical mechanics, where the basic connections between micro and macro are sought in ergodic theorems. These suppose that the microstate will eventually pass near every one compatible with the total macroscopic energy; if so, then the then the long-time*

behavior of a system must be determined by its energy. What we see about us does not suggest this." In order to find an alternative, and possibly more elegant procedure, let us turn the question around, starting now from Gibbs original work. We quote again a sentence of Jaynes (1985): *"Why is that knowledge of microphenomena does not seem sufficient to understand macrophenomena? Is there an extra general principle needed for this? Our message is that such a general principle is indeed needed and already exists, having been given by J. Willard Gibbs 110 years ago... . A macrostate has a crucially important further property - entropy - that is not determined by the microstate."*

We will show now that all Gibbsian ensembles may be derived in a unique way just from one principle, the *Gibbs-Jaynes maximum entropy principle*. We start as Gibbs and Jaynes from a very general variational principle. In order to explain this variational principle we start with the following abstract problem: We consider a macroscopic systems, given incomplete information A. Then we postulate that holds the

Gibbs-Jaynes principle:

If an incomplete information A is given about a macroscopic system, the best prediction we can make of other quantities are those obtained from the "ensemble" ρ that has maximum information entropy H while agreeing with A. By "agreeing" with A we mean that the average $< A >$ calculated with ρ corresponds to the given information A.

Let us sketch briefly how this general principle works in the case that $\rho = \rho(q,p)$ is a probability density in the phase space and $A = [A_1, ..., A_m]$ stands for a set of real functions on the phase space. The most important case is that the $A_k(q,p)$ are constants of the motion (energy, angular momentum, particle numbers etc.). In order to find the probability density under the constraints

$$A'_k = \langle A_k \rangle = \int dq dp A_k(q,p)\rho(q,p) \tag{4.51}$$

we maximize the information entropy

$$\mathcal{H} = -\int dq dp \rho(q,p) \ln \rho(q,p) \tag{4.52}$$

under the given constraints. We define an m-component vector $\lambda = [\lambda_1, ..., \lambda_m]$ of Lagrange multipliers. Then the probability density that agrees with the given data $\mathbf{A}'$ follows from

$$\delta[\mathcal{H} + \sum_k \lambda_k(A'_k - \int dq dp A_k(q,p)\rho(q,p))] = 0 \tag{4.53}$$

This leads to

$$\rho(q,p) = Z^{-1} \exp[-\sum_k \lambda_k A_k(q,p)], \tag{4.54}$$

where the normalization factor, the so-called partition function, is given by

$$Z(\lambda_1, ..., \lambda_m) = \int dq dp \exp[-\sum_k \lambda_k A_k(q, p)] \tag{4.55}$$

The found probability density ρ spreads the probability as uniformly as possible over all microstates subject to the constraints. The Lagrange multipliers are found from the relations

$$A'_k = \langle A_k \rangle = -\frac{\partial}{\partial \lambda_k} \ln Z(\lambda_1, ..., \lambda_m). \tag{4.56}$$

The dispersion is given by second derivatives

$$\langle (A_k - A'_k)^2 \rangle = \frac{\partial^2}{\partial \lambda_k^2} \ln Z(\lambda_1, ..., \lambda_m) = -\frac{\partial}{\partial \lambda_k} \langle A_k \rangle \tag{4.57}$$

We see that the linear 'ansatz' (4.54) implies that the mean values and the dispersion are closely connected. Let us turn now to more concrete examples:

- Microcanonical ensemble:
  The case that there are no constraints, except the fixation of the system on an energy shell. This leads to the ensemble (on the shell)

$$\rho(q, p) = const. \tag{4.58}$$

- Canonical ensemble:
  The case that the mean of the energy is given $A'_1 = E = \langle H \rangle$ leads to the ensemble

$$\rho(q, p) = Z^{-1} \exp[-\beta H(q, p)]. \tag{4.59}$$

- Grand canonical ensemble:
  The case that besides the mean energy $A'_1 = E$ also the s mean particle numbers are given $A'_2 =< N_1 >, ..., A'_{s+1} =< N_s >$ are given leads to the ensemble

$$\rho(q, p; N_1, ..., N_s) = Z^{-1} \exp[-\beta H(q, p) - \lambda_1 N_1 - ... - \lambda_s N_s]. \tag{4.60}$$

  After identifying β with the reciprocal temperature and λ_k/β with the chemical potentials, we are back at the formulae derived in the last section.

- Canonical ensemble for rotating bodies:

We consider here the case of rotating bodies consisting of N particles in internal equilibrium. We assume that the angular velocity of the body is ω and the angular momentum is $\mathbf{L}$. In a coordinate system which rotates with the body we find the Hamiltonian

$$H_r = H - \mathbf{\Omega} \cdot \mathbf{L} \tag{4.61}$$

The assumption that in the rotating system the system behaves like a standard canonical ensemble we find (Landau & Lifshits, 1990)

$$\rho(q, p) = Z_r^{-1} \exp[-\beta H_r(q, p)]. \tag{4.62}$$

This leads in the original system of coordinated to the distribution

$$\rho(q, p) = Z^{-1} \exp\left[-\beta \left(H(q, p) - \mathbf{\Omega} \cdot \mathbf{L}(\mathbf{q}, \mathbf{p})\right)\right]. \tag{4.63}$$

This distribution may be obtained directly from Jaynes method by assuming that $\mathbf{L}$ plays the role of an additional observable which is an integral of motion and Ω is the corresponding Langrange parameter, connected with the mean value of the angular momentum by

$$\langle \mathbf{L} \rangle = -\beta^{-1} \frac{\partial}{\partial \mathbf{\Omega}} \ln Z(\beta, \mathbf{\Omega}). \tag{4.64}$$

This way we have shown that the Gibbs-Jaynes maximum entropy principle is indeed very powerful, it contains all known distributions for equilibrium situations as special cases. In fact, the principle provides much more useful information (Levine & Tribus, 1978). A few other applications, including non-equilibrium situatations, will be demonstrated below. In non-equilibrium, in general, the linear 'ansatz' (4.54) is no more sufficient, since the means and the dispersion may be independent variables. In order to admit such situations we have to use quadratic functions in the exponent of the distribution function. Examples will be demonstrated in the next Chapter.

Chapter 5

Fluctuations and Linear Irreversible Processes

5.1 Einstein's theory of fluctuations

In this chapter we will present several aspects of the statistical theory of fluctuations and the theory of linear irreversible processes (Haase, 1963; Prigogine, 1967, Keller, 1977; DeGroot & Mazur, 1984, Schwabl, 2000, Schimansky-Geier & Talkner, 2002). This theory is a well developed part of the statistical physics which holds true close to equilibrium. The main result of the statistical theory near to equilibrium is the foundation of a deep connection between fluctuations and dissipation, both phenomena seemingly not related one to the other. This insight is due mainly to the work of Einstein and Onsager. One of our main topics is the study of the interaction of the degree of freedom under consideration with the surrounding. In this relation the concrete way of interaction with the particles or dynamic modes of the surrounding is not of interest for the description of the relevant variables. This interaction causes dissipation, i.e. the distribution of concentrated energy to many degrees of freedom and causes deviations from the equilibrium states, fluctuations. Thus as will be shown, the correlation functions and spectra of the fluctuations stand in close relation to the response function on external forces, to the dissipative and transport coefficients as long as the linear approximation around an equilibrium states holds. Unfortunately the extension of this beautiful theory to all systems far from equilibrium is impossible.

The *Boltzmann-Planck principle* developed in Section 4.1 was generalized by Einstein and applied to fluctuations in several seminal papers published in 1902-1906. Suppose that x should be a fluctuating quantity of a thermodynamic system. Taking the general view of statistical physics, we will assume that x is an explicit function of the microscopic variables.

$$x = x(q_1, ..., p_f). \qquad (5.1)$$

Suppose further on that we deal with an isolated thermodynamic system, i.e. E, N, V are

(macroscopic) constants. We want to find the probability distribution $w(x)$ of the fluctuating value x under the given isoenergetic conditions. The key for the solution of this problem is the statistical definition of the thermodynamic entropy due to Boltzmann and Planck (see Section 4.1). Under the assumption of thermodynamic equilibrium at fixed E, V, N we will introduce a conditional entropy $S(x|E, V, N)$ for the microscopic states where a certain value of x is realized. Geometrically the form $x = const$ is some subset of the hypersurface $E = const.$. Therefore, this entropy is determined by the number of microscopic states or in other words by the thermodynamic weight $\Omega(x|E, V, N)$ of the states which correspond to the value of x:

$$S(x|E, V, N) = k_B \ln \Omega(x|E, V, N). \tag{5.2}$$

The probability distribution to find a certain value of x is then defined by

$$\omega(x|E, V, N) = \frac{\Omega(x|E, V, N)}{\Omega(E, V, N)} \tag{5.3}$$

or respectively according to (5.1)

$$\omega(x) = \exp\left[-\frac{1}{k_B T}\left(S(E, V, N) - S(x|E, V, N)\right)\right]. \tag{5.4}$$

Therefore we reduced the information on the thermodynamic system to the knowledge of the distribution of x. The main idea in Einstein's approach consists in the calculation of the entropy difference δS for two states based on thermodynamic relations, i.e. the Gibbsian fundamental equation. Additionally since (5.4) is a normalized distribution we do not have to know the full thermodynamic entropy $S(E, N, V)$, but just relative changes. Further on we set $S(x|E, V, N) = S(x)$. Then obviously, is true that

$$\omega(x) = \frac{\exp[S(x)/k_B]}{\int dx \exp[S(x)/k_B]}. \tag{5.5}$$

The same result may be obtained by application of a projection technique. By introducing a δ-function we collect the microscopic probability corresponding to the value x. The conditional entropy (5.2) then reads

$$S(x|E, N, V) = k_B \ln \int d\Gamma \delta(x - x(q_1, ..., p_{3N}))\delta(H - E) \tag{5.6}$$

The probability distribution follows respectively

$$\omega(x) = \exp[-S(E, V, N)/k_B] \cdot \int d\Gamma \delta(x - x(q_1, ..., p_{3N}))\delta(H(q_1, ..., p_{3N}) - E) \tag{5.7}$$

This expression is equivalent to the distribution (5.4). The present approach can also be applied to microscopic distributions under different thermodynamic constraints. For example, if x is a fluctuating value of an isothermic-isochoric system the projection procedure yields

$$\omega(x|T, V) = \exp\left[\frac{F(t, V)}{k_B T} - \frac{F(x|T, V)}{k_B T}\right] \tag{5.8}$$

where

$$F(x|T,V) == -kT \ln \int d\Gamma \delta(x - x(q_1, ..., p_{3N})) \exp\left[-H(q_1, ..., p_{3N}/k_BT\right] \tag{5.9}$$

is the conditional free energy for the isothermic-isochoric system under the condition that x is fixed.

Let us list some general properties of the probability distribution near equilibrium. First of all looking for distributions of x around the equilibrium value x_0 the thermodynamic potentials have extremal properties with respect to x. From the second law follows $S \rightarrow max$, the maximum is reached in equilibrium, i.e. if x reaches the value x_0. Therefore an expansion around a stable equilibrium state gives

$$S(x) = S(x_0) - \frac{1}{2}k_B\beta(x - x_0)^2 \tag{5.10}$$

with

$$\beta = -\frac{1}{k_B}\left(\frac{\partial^2 S}{\partial x^2}\right) > 0. \tag{5.11}$$

This way we obtain that the fluctuations around equilibrium states are Gaussian.

$$\omega(x) = \sqrt{\frac{\beta}{2\pi}} \exp\left[-\frac{1}{2}\beta(x - x_0)^2\right] \tag{5.12}$$

The standard deviations are determined by the second derivatives of the entropy

$$\langle (x - x_0)^2 \rangle = 1/\beta \tag{5.13}$$

For other thermodynamic embeddings we obtain in an analogous way Gaussian distributions where β is the positive second derivative of the corresponding thermodynamic potential. As a concrete example we derive the distribution of the fluctuating position of a mechanical spring. It is surrounded by a gas and both the spring and the gas should be in equilibrium under the condition that the overall energy is constant. The change of the entropy of the overall system (gas and spring) can be calculated using the concept of the reversible *"Ersatzprozess"*. It yields for small deviations

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE = -\frac{1}{T}dW_{min} \tag{5.14}$$

where W_{min} is the required minimal reversible work which has to be applied to bring the spring out off equilibrium. In our case, if x_0 is the equilibrium position and χ the elasticity

$$dS = -\frac{1}{T}\chi(x - x_0)dx \tag{5.15}$$

Therefore we arrive at

$$\omega(x) = \sqrt{\frac{\chi}{2\pi k_BT}} \exp\left[-\frac{\chi(x - x_0)^2}{2k_BT}\right]. \tag{5.16}$$

This formula played an important for the experimental determination of the Boltzmann constant k_B.

5.2   Fluctuations of many variables

In the case that there are several fluctuating variables $x_1, ..., x_s$, the variable x may be treated as a vector $\boldsymbol{x}$ with components $x_i, (i = 1...n)$ (Klimontovich, 1982, 1986). The resulting Gaussian distribution near the equilibrium state $\boldsymbol{x}_0$ reads

$$\omega(\boldsymbol{x}) = \sqrt{\frac{det\boldsymbol{\beta}}{(2\pi)^n}} \exp\left[-\frac{1}{2}\sum \beta_{ij}(x_i - x_{i0})(x_j - x_{j0})\right] \tag{5.17}$$

with the matrix

$$\beta_{ij} = -\frac{1}{k_B}\left(\frac{\partial^2 S}{\partial x_i x_j}\right) \tag{5.18}$$

and the second moments

$$\langle(x_i - x_{i0})(x_j - x_{j0})\rangle = (\beta^{-1})_{ij}. \tag{5.19}$$

As an application we determine now the fluctuations of the thermodynamic variables T, V, N etc. of a subvolume which is embedded into a thermal bath with temperature T. Both bath and subvolume together should be adiabatically isolated, i.e. their common energy, volume and particle number E, V, N are constants. Two standard problems are:
i) V is fluctuating and N is fixed, or
ii) N is fluctuating and V is fixed.
Here N, V denote the particle number and volume of the subvolume respectively. We have to calculate the entropy change of an occurring fluctuation taking into account the thermodynamic constraints. If the subvolume is a macroscopic body, this entropy change consists of two parts coming from the subvolume and from the bath, respectively

$$\Delta S_{total} = \Delta S + \Delta S_b. \tag{5.20}$$

First we let V be fluctuating and the particle number of the subvolume N be conserved. Conservation of the overall volume and energy makes the entropy change of the bath to be a function of the values for the subvolume

$$\Delta S_b = \frac{\Delta E_b + p_b \Delta V_b}{T_0} = -\frac{\Delta E + p_0 \Delta V}{T_0}. \tag{5.21}$$

Further we expand ΔE in a series for small deviations of the entropy and the volume from its equilibrium values.

$$\Delta E = T_0 \Delta S - p_0 \Delta V + \frac{1}{2}(\Delta T \Delta S - \Delta p \Delta V) \tag{5.22}$$

Combining these relations we find in quadratic approximation the probability for occurring fluctuations of the thermodynamic variables

$$W = A\exp\left[\frac{\Delta p \Delta V - \Delta T \Delta S}{2k_B T_0}\right] \tag{5.23}$$

Analogously we get for a fixed subvolume and a fluctuating particle number

$$W = A \exp\left[-\frac{\Delta\mu\Delta N + \Delta T\Delta S}{2k_B T_0}\right]. \tag{5.24}$$

We mention that in both cases the values in the exponents correspond to the negative minimal work which has to be applied to bring the subvolume to the nonequilibrium state with $\Delta T, \Delta S$ etc.. Now we remember that the deviations from equilibrium are not independent one from each other near to equilibrium. In both expressions only two variable are independent and will govern the behavior of the remaining variables by the caloric and thermic state equation. Selecting in (5.23) ΔT and ΔV as independent variables it determines the behavior of ΔS and Δp

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta p, \tag{5.25}$$

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_V \Delta T + \left(\frac{\partial p}{\partial V}\right)_T \Delta V. \tag{5.26}$$

This way we get the formula

$$W(\Delta T, \Delta V) = A \exp\left[-\frac{C_V}{2k_B T_0^2}(\Delta T)^2 + \frac{1}{2k_B T}\left(\frac{\partial p_0}{\partial V_0}\right)_{T_0}(\Delta V)^2\right]. \tag{5.27}$$

Several interesting questions can be discussed on the basis of this expression:
First of all we see that in the linear approximation near equilibrium, extensive and intensive thermodynamic variables are decoupled. This follows from

$$\langle \Delta T \Delta V \rangle = 0 \tag{5.28}$$

and equivalently for the combination of the other variables. Further on the standard deviations of intensive variables scale with

$$\langle (\Delta T)^2 \rangle = \frac{k_B T_0^2}{C - V} \simeq \frac{1}{V_0} \tag{5.29}$$

For extensive variables the same scaling is found for the mean square deviations of relative quantities, e.g.

$$\frac{\langle (\Delta V)^2 \rangle}{V_0^2} = k_B T_0 \frac{K_T}{V_0} \tag{5.30}$$

Here K_T denotes the relative isothermic expansion coefficient

$$K_T = -\frac{1}{V_0}\left(\frac{\partial V_0}{\partial p_0}\right)_{T_0}. \tag{5.31}$$

A third point we want to discuss is the question of thermodynamic stability. Positivity of C_V and K_T is a consequence from thermodynamic inequalities resulting from the second law. Allowing additionally fluctuation of the thermodynamic variables equilibrium is defined as the maxima of the corresponding distributions. For the particle number fluctuations we find starting from (5.24)

$$\langle (\Delta N)^2 \rangle = k_B T_0 \left(\frac{\partial N_0}{\partial \mu_0} \right)_{T_0, V_0}. \tag{5.32}$$

This relation is in close relation to the stability of thermodynamic phases upon the variation of particle numbers.

5.3 Onsager's theory of linear relaxation processes

According to Einstein's view, any macroscopic quantity x may be considered as a fluctuating variable, which is determined by certain probability distribution $\omega(x)$. The mean value is given as the first moment of the probability distribution

$$x_0 = < x > = \int x \cdot \omega(x) dx. \tag{5.33}$$

In a stationary state we may shift the origin and assume $x_0 = 0$, without loss of generality. Let us assume now that the stationary state, the target of our investigation, is the state of thermodynamic equilibrium. Then $x_0 = 0$ corresponds to equilibrium and any value of $x(t)$ different from zero is strictly speaking a nonequilibrium state. According to the 2nd Law, there exists a Lyapunov function and therefore the equilibrium state is an attractor of the dynamics (see section 2.2). The equilibrium state corresponds to a maximum of the entropy. This means in the present situation:

$$S(x = 0) = max; \tag{5.34}$$

$$\left(\frac{\partial S}{\partial x} \right)_{x=0} = 0; \qquad \left(\frac{\partial^2 S}{\partial x^2} \right)_{x=0} \leq 0. \tag{5.35}$$

According to Onsagers's view, the relaxation dynamics of the variable x is determined by the first derivative of the entropy, which is different from zero outside equilibrium. Starting from a deviation from the equilibrium (an entropy value below the maximum) the spontaneous irreversible processes should drive the entropy to increase

$$\frac{d}{dt} S(x) = \frac{\partial S}{\partial x} \cdot \frac{dx}{dt} \geq 0. \tag{5.36}$$

In this expression two factors appear, which were interpreted by Onsager in a quite ingenious way. According to Onsager the derivative

$$X = -\frac{\partial S}{\partial x} \tag{5.37}$$

is considered as the driving force of the relaxation to equilibrium. In irreversible thermodynamics this term is called in analogy to mechanics the *thermodynamic force*, the analogy means that the (negative) entropy takes over the role of a potential. The second term

$$J = -\frac{dx}{dt} \tag{5.38}$$

is considered as the *thermodynamic flux* or *thermodynamic flow*. In a seminal paper, concerned with the question of the relaxation of nonequilibrium states to equilibrium, Onsager (1931) postulated a linear relation between the thermodynamic force and the flux

$$J = LX \tag{5.39}$$

The idea behind is, that the thermodynamics force is the cause of the thermodynamic flow and both should disappear at the same time. The coefficient L is called *Onsager's phenomenological coefficient*, or *Onsager's kinetic coefficient*. From the 2nd Law follows that the Onsager-coefficients are strictly positive.

$$P = \frac{d}{dt}S(x) = J \cdot X = L \cdot X^2 \geq 0 \tag{5.40}$$

Onsager's postulate about a linear connection between thermodynamic forces and fluxes is the origin of the development of the thermodynamics of linear dissipative system, called also *linear irreversible thermodynamics*. A remarkable property of the linear theory is the bilinearity of the entropy production

$$P = J \cdot X \tag{5.41}$$

Referring now to the fluctuation theory eq.(5.10) we find for the neighborhood of the equilibrium state the relation

$$X = -\frac{\partial S}{\partial x} = k_B \beta x \tag{5.42}$$

Using the previous equations we get finally the following linear relaxation dynamics

$$\dot{x} = -k_B L \beta x. \tag{5.43}$$

With the abbreviation

$$\lambda = L k_B \beta \tag{5.44}$$

being the so-called *relaxation coefficient* of the quantity x we get finally

$$\dot{x} = -\lambda x \tag{5.45}$$

This linear kinetic equation describes the relaxation of a thermodynamic system brought initially out of equilibrium. Starting with the initial state $x(0)$ the dynamics of the variable $x(t)$ is

$$x(t) = x(0) \exp[-\lambda t]. \tag{5.46}$$

We see that $t_0 = \lambda^{-1}$ plays the role of the decay time of the initial deviation from equilibrium. On the other hand this coefficient which is responsible for the relaxation to equilibrium is in close relation to the fluctuation properties of the considered system. Indeed eq.(5.44) connects a kinetic property λ with a fluctuation quantity β. In this way we arrived for the first time at a so-called fluctuation-dissipation relation. In fact, Onsager assumed that deviations from equilibrium and fluctuations around the equilibrium observe the same kinetics.

Quite similar we might proceed if we are dealing with several thermodynamic values. Indeed taking the entropy in dependence on $x_i, (i = 1...N)$ the entropy production reads

$$S(x_1, ..., x_n) = S_{max} - \frac{1}{2}\beta_{ij}x_i x_j. \tag{5.47}$$

We agree, here and further on, to sum over repeating indices (Einstein's convention).

Following the Onsager ideas described above we get for the thermodynamic forces and fluxes the relations

$$X_i = -k_B \beta_{ij} x_j \tag{5.48}$$

$$J_i = -\dot{x}_i \tag{5.49}$$

The generalized linear Onsager-ansatz reads

$$J_i = L_{ij} X_j. \tag{5.50}$$

Again the 2nd law requires positivity of the entropy production. This requires

$$L_{ij} X_i X_j \geq 0 \tag{5.51}$$

for any value of X_i and disappearance only for $X_i = 0, i = 1, ..., n$. This corresponds to the requirement of positive definiteness of the matrix L_{ij}. By inserting eqs.(5.48) and (5.49) into eq.(5.50) we get

$$\dot{x}_i = -k_B L_{ij} X_j, \tag{5.52}$$

and introducing the matrix of relaxation coefficients of the linear processes near equilibrium states we end up with

$$\dot{x}_i = -\lambda_{ij} x_j, \tag{5.53}$$

$$\lambda_{ij} = k_B L_{ik} \cdot \beta_{kj}. \tag{5.54}$$

Since the matrix β_{ij} determines the dispersion of the stationary fluctuations, we have found again a close relation between fluctuations and dissipation, i.e. we have got a fluctuation-dissipation relation for a set of fluctuating and relaxing variables.

5.4 Correlations and spectra of stationary processes near equilibrium

This section is devoted to the time correlation functions and their spectrum (Klimontovich, 1982, 1986; Schimansky-Geier & Talkner, 2002). The time correlation functions will be defined here as averages over the stationary probability distribution $\omega(x)$. We consider only stationary processes and the corresponding stationary probability distributions. As a consequence of stationarity all characteristic functions depending on two times t, t' are functions of their time difference $t - t'$ only. We define the correlation function of a variable $x(t)$ as the mean over the product with the same function taken at a later time.

$$C(\tau) = < x(t)x(t+\tau) >_t = \int dx \omega(x) x(t) x(t+\tau); \qquad \tau > 0 \tag{5.55}$$

There are two equivalent ways of definition:
(i) the time average over a long (infinite) time interval,
(ii) an ensemble average based on certain probability distribution $\omega(x)$.
For the case of many fluctuating variables $x_i(t), (i = 1, ... n)$ the time correlation function is defined as

$$C_{ij}(\tau) = < x_i(t)x_j(t+\tau) >_t = \int dx_1 ... dx_n \omega(x_1, ..., x_n) x_i(t) x_j(t+\tau) \tag{5.56}$$

where $\tau > 0$ and $\omega(x_1, ..., x_n)$ stands for the simultaneous probability distribution of all x_i-variables.
We will study now several general properties of the time correlation functions.

- The first (evident) property is:
  The time correlation functions should vanish for infinitely large time and be equal to the covariance coefficient for small time

$$\lim_{t \to \infty} C_{ij}(\tau) = 0; \qquad C_{ij}(\tau = 0) = \langle x_i x_j \rangle \tag{5.57}$$

- A second property follows immediately from the stationarity: Since $C_{ij}(\tau)$ does not depend on the actual time we find by substituting $t \to t' - \tau$

$$C_{ij}(\tau) = < x_i(t)x_j(t+\tau) > = < x_i(t'-\tau)x_j(t') > = C_{ji}(-\tau). \tag{5.58}$$

We introduce now the Fourier-component of the time correlation function

$$S_{ij}(\omega) = \int_{-\infty}^{\infty} d\tau C_{ij}(\tau) \exp[i\omega\tau]. \tag{5.59}$$

This matrix function is called the spectrum of the fluctuating values. It can be calculated directly from the time correlation function via eq.(5.59). Another way is by the analysis of the dynamics of the fluctuating values. We introduce first the Fourier-components of $x_i(t)$

$$x_{i\omega} = \int_{-\infty}^{+\infty} dt x_i(t) \exp[i\omega t]. \tag{5.60}$$

We multiply this expression with $x_{j\omega}$ and average over the stationary distribution

$$< x_{i\omega} x_{j\omega'} > = \int \int_{-\infty} +\infty dt dt' < x_i(t) x_j(t') > \exp[i(\omega + \omega')t + i\omega'(t' - t)]. \tag{5.61}$$

Due to the stationarity the correlator $< x_i(t) x_j(t') >$ depends on the difference $t' - t$

$$< x_{i\omega} x_{j\omega'} > = 2\pi\delta(\omega + \omega') S_{ij}(\omega). \tag{5.62}$$

This is a form of the *Wiener-Khintchin-theorem* which connects the averaged product of the modes of a fluctuating stationary system with the spectrum of the fluctuating values. Later on we will make use of this equation.

In the last section we derived equations for the linear relaxation dynamics of macroscopic variables. Onsager stated that these equations are valid for the relaxation of fluctuations too. Indeed, in the derivation of the relaxation dynamics we never made a statement whether the initial nonequilibrium state has been prepared, as a result of an external force like usually by considering the dynamics of mean values or as the result of a spontaneous fluctuation. This way Onsager postulated the validity of these equations for the regression of fluctuating variables. As a consequence we may calculate the dynamic characteristics of fluctuations like the time correlation function from the relaxation kinetics. There exist several approaches to prove the Onsager postulate (Klimontovich, 1982, 1986, 1995; Landau & Lifshits, 1990), we take it here as a quite evident hypothesis.

In order to calculate the correlation functions we start from the relaxation equations for the variables $x_i(t)$ which reads in the simplest case of one component $\dot{x}(t) = -\lambda x(t)$ (see previous section). We assume now that this relation is valid also for a deviation caused by a spontaneous fluctuation. We multiply the relaxation equation with the initial value $x(0)$ and find

$$\frac{d}{dt}(x(t)x(0)) = -\lambda(x(t)x(0)) \tag{5.63}$$

After averaging with respect to an ensemble of realizations we get a kinetic equation for the time correlation function

$$\frac{d}{d\tau} C(\tau) = -\lambda C(\tau) \tag{5.64}$$

with the initial conditions

$$C(\tau = 0) = < x^2 > = \int x\omega dx = \beta^{-1}. \tag{5.65}$$

By integrating (5.64) we find the explicit expression for the correlation function

$$C(\tau) = \frac{1}{\beta}\exp[-\lambda|\tau|] \tag{5.66}$$

The generalization to several fluctuating variables is straightforward. The application of Onsager's regression hypothesis leads to the kinetic equations

$$\frac{d}{d\tau}C_{ij}(\tau) = -\lambda_{ik}C_{kj} \tag{5.67}$$

with the initial condition

$$C_{ij}(0) = <x_i x_j>. \tag{5.68}$$

The most elegant method to solve these equations are one-sided Fourier-transforms (Klimontovich, 1984). We represent the time correlation functions as

$$S_{ij}^+(\omega) = \int_0^\infty d\tau C_{ij}(\tau)\exp[i\omega\tau] \tag{5.69}$$

The negative part of the spectrum is just the complex conjugate

$$S_{ij}^-(\omega) = \int_{-\infty}^0 d\tau C_{ij}(\tau)\exp[i\omega\tau] = [S_{ij}^+(\omega)]^* \tag{5.70}$$

Taking into account the initial conditions we find for the positive part

$$(-i\omega\delta_{ik} + \lambda_{ik})S_{kj}^+(\omega) = <x_i x_j> \tag{5.71}$$

From here on we consider C_{ij} and λ_{ik}, and $S_{ij}^\pm$ as elements of matrices $\mathbf{C}$ and Λ and $\mathbf{S}^\pm$. We moreover introduce the matrix $\mathbf{B} = \mathbf{C}^{-1}(0)$, and use the notation $\mathbf{I}$ for the unit matrix with elements δ_{ij}.

By adding positive and negative parts we get the complete spectrum

$$\mathbf{S}(\omega) = (-i\omega\mathbf{I} + \Lambda)^{-1}\mathbf{B}^{-1} + \mathbf{B}^{-1}(-i\omega\mathbf{I} + \Lambda)^{-1}. \tag{5.72}$$

Here we have used the matrix inversion of eq.(5.71) and the symmetry relation $C_{ij}(\tau) = C_{ji}(-\tau)$, valid for stationary processes. The correlation function $C_{ij}(\tau)$ follows from the inverse Fourier transform.

In order to illustrate this procedure we take as a simple example Brownian motion, i.e. the motion of a heavy particle in a viscous liquid. As well known, this problem was first studied 100 years ago by Albert Einstein in one of his seminal papers in Annalen der Physik (**17**, 549-560 (1905)). In the next Chapters we will study Brownian motion in more detail. here we look only

at its connection with the theory of linear irreversible processes. We assume for the velocity of the particle the linear equation of motion

$$\dot{v} = -\gamma_0 v. \tag{5.73}$$

For the stationary correlation function we get

$$\frac{d}{d\tau} < v(t+\tau)v(t) > = -\gamma_0 < v(t+\tau)v(t) > \tag{5.74}$$

with the initial condition

$$< v(t)^2 > = \frac{k_B T}{m}. \tag{5.75}$$

Solving these equations we find the correlation function of Brownian particles

$$< v(t+\tau)v(t) > = \frac{k_B T}{m} \exp[-\gamma|\tau|] \tag{5.76}$$

with the spectrum

$$S_{vv}(\omega) = \frac{k_B T}{m} \frac{2\gamma_0}{\gamma_0^2 + \omega^2}. \tag{5.77}$$

Sometimes this frequency distribution is called a red spectrum, since the maximum of intensity is at low ω. A more rich structure of the spectrum is obtained if the particle is additionally under the influence of a harmonic force. Then the dynamical equations read

$$\dot{x} = v; \qquad \dot{v} = -\gamma_0 v - \omega_0^2 x \tag{5.78}$$

and the corresponding system of equations for the correlation functions is

$$\dot{C}_{xv}(\tau) = C_{vv}(\tau); \qquad \dot{C}_{vv} = -\gamma_0 C_{vv} - \omega_0^2 C_{xv}. \tag{5.79}$$

Following the approach described above we find the spectrum

$$S_{vv}(\omega) = \frac{k_B T}{m} \frac{2\gamma_0}{\gamma_0^2 + (\omega - \omega_0^2/\omega)^2}. \tag{5.80}$$

This distribution has a peak at $\omega \simeq \omega_0$, a so-called resonance. Details and applications will be discussed in subsequent Chapters.

5.5   Symmetry relations and generalizations

At the end of this chapter we want to come back to the Onsager matrix of phenomenological coefficients L_{ij}, relating the thermodynamic fluxes and forces near to equilibrium. Empirically

it was found that the matrix is symmetrical with respect to exchange of the indices and in a few cases one observes antisymmetry

$$L_{ji} = \pm L_{ij}. \tag{5.81}$$

This macroscopic property means that if a force X_j will induce the thermodynamic flux J_i we will find also a flux J_j generated by the force X_i. This circumstance, was also found already in Onsager's paper.

For the proof of this relation we use properties of the correlation function, in particular $C_{ij}(\tau) = C_{ji}(-\tau)$. The second fact which has to be taken into account is that the fluctuating values are functions of the microscopic variables. Therefore it holds

$$x_i(t) = \epsilon_i x_j(-t) \tag{5.82}$$

which expresses the reversibility of the microscopic motion. Here ϵ is the parity coefficient which is $+1$ for even variables and -1 for odd ones. It yields that

$$C_{ij}(\tau) = < x_i(t)x_j(t+\tau) > = \epsilon_i\epsilon_j < x_i(-t)x_j(-t-\tau) > = \epsilon_i\epsilon_j C_{ij}(-\tau). \tag{5.83}$$

Taking into account the stationarity condition we find

$$C_{ij}(\tau) = \epsilon_i\epsilon_j C_{ji}(\tau). \tag{5.84}$$

As a consequence of the general regression dynamics we find the following dynamical equations for the correlation functions

$$\frac{d}{d\tau}C_{ij}(\tau) = -\lambda_{ik}C_{kj}(\tau). \tag{5.85}$$

Hence we obtain

$$\lambda_{ik}C_{kj}(\tau) = \epsilon_i\epsilon_j\lambda_{jk}C_{ki}(\tau). \tag{5.86}$$

For $\tau = 0$ the correlation function reduces to the standard deviation with $C_{ij}(0) = [\beta_{ij}]^{-1}$; using further the definition of the relaxation coefficients λ_{ij} we get finally the famous *Onsager-Casimir symmetry relation*

$$L_{ji} = \epsilon_i\epsilon_j L_{ij}. \tag{5.87}$$

This relation is one of the fundamentals of linear irreversible thermodynamics; it is well confirmed by many experiments.

The approach presented so far in this Chapter is restricted to irreversible processes close to equilibrium. The extension to far from equilibrium situations is extremely difficult. There exist many approaches to solve this problem. We mention the early work of Onsager and Machlup (1953), of Machlup and Onsager (1953), of Ginzburg and Landau (1965), and of Glansdorff and Prigogine (1971). An advanced theory of nonlinear irreversible processes is due to the work of the late Rouslan Stratonovich (Stratonovich, 1994). We mention also the

extended thermodynamics and other new approaches (Muschik, 1988; Jou, Casas-Vazques & Lebon, 1993; Ebeling & Muschik, 1993; Luzzi, Vasconcellos & Ramos, 2000). Special attention deserves a new approach (Grmela & Öttinger, 1997), named GENERIC (general equations for the nonequilibrium reversible-irreversible coupling), which seems to contain most of the theories mentioned above as special cases (Öttinger, 2005). We will give here only one of the basic ideas. The general time-evolution equation postulated by Grmela and Öttinger is of the following structure:

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}. \tag{5.88}$$

Here x represents a set of independent variables, in many cases x will depend on continuous position-dependent fields, such as mass, momentum, and energy densities. Further, E and S are the total energy and entropy expressed in terms of the state variables, and L and M are certain linear operators or matrices. The application of a linear operator may include integrations over continuous labels and then $\delta/\delta x$ typically implies functional rather than partial derivatives. There is no room here to go into the details of these more or less fruitful but not exhaustive methods. The whole field is still in development.

Chapter 6

Nonequilibrium Distribution Functions

6.1   A simple example – driven Brownian particles

The general theory of nonequilibrium systems is still in the first stages of development. At present we have a well developed theory of ideal gases going back to *Boltzmann*. We presented the main ideas of this rather old theory already in the 3rd Chapter. Further we have a nice theory for small (linear) deviations from equilibrium, which essentially goes back to Einstein and Onsager, this theory was presented in Chapter 5. A theory of the same generality as the Gibbs theory of equilibrium systems does not exist yet. In particular the formulation of the statistical mechanics of far-from equilibrium systems is an extremely difficult task which is full of surprises and interesting applications to many interdisciplinary fields (Haken, 1973, 1983; Klimontovich, 1995: Zubarev, 1976: Schimansky-Geier & Pöschel, 1997). On the other hand we may treat many special examples, several of them will presented in this and in the following sections. We will start again with a treatment of Brownian motion and related phenomena and will finish this Chapter with general information-theoretical methods.

In order to bring a system to nonequilibrium we need some driving force. Historically the first case of a treatment of driven systems is connected with the theory of sound developed in the 19th century by Helmholtz and Rayleigh. The treatment of these early models will lead us later to other interesting applications as the theory of driven Brownian particles. This is a unification of the model of Brownian motion due to Einstein, Smoluchowski and Langevin with the model of (acoustic) oscillators driven by negative friction developed by Rayleigh, Helmholtz, van der Pol and many other workers. We will use here the definitions and results introduced in Sections 2.4 and 2.5.

Let us study at the beginning a force-free Brownian particles on a line ($d = 1$) under equilibrium conditions. Using the phenomenological method we find the Maxwellian distribution,

which is a special case of the canonical distribution function defined in sections 4.3-4.4:

$$f_0(\mathbf{v}) = \rho(H) = C \exp\left[-\frac{mv^2}{2k_BT}\right]. \tag{6.1}$$

There is an alternative method to derive this distribution based on the Langevin-Fokker-Planck method. We start from the Langevin equation (see section 2.5)

$$\frac{dv}{dt} = -\gamma_0 v + (2D_v)^{1/2}\xi(t) \tag{6.2}$$

which describes standard Brownian motion in equilibrium systems (γ_0 - friction coefficient, D_v-diffusion constant for the velocities). The corresponding Fokker-Planck equation reads (see section 2.5)

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial v}\left[\gamma_0 v P(v,t) + D_v \frac{\partial P(v,t)}{\partial v}\right] \tag{6.3}$$

This equation is solved by the Gaussian distribution

$$f_0(v) = C \exp\left[-\frac{\gamma_0 v^2}{2D_v}\right]. \tag{6.4}$$

The Gaussian corresponds to the equilibrium Maxwell distribution just in the case that the so-called *Einstein relation*

$$D_v = \frac{k_B T \gamma_0}{m} \tag{6.5}$$

holds. This case will be studied in more detail in Chapters 6-9. Here we are more interested in the transition to non-equilibrium situations when eqs.(6.4) and (6.5) are not observed. In this case the system might be driven away from equilibrium; then we speak about active Brownian motion. The corresponding Langevin equation of motion reads ($m = 1$):

$$\frac{dv}{dt} = F(v) + (2D(v))^{1/2}\xi(t) \tag{6.6}$$

Here $F(v)$ is the dissipative force acting on the particle and $D(v)$ a diffusion function. The simplest case

$$F(v) = -\gamma_0 v; \qquad D(v) = D_v = const \tag{6.7}$$

leads as back to standard Brownian motion. Now we will consider nonequilibrium situations corresponding to nonlinear expressions for the force. Models of nonlinear dissipative forces were first considered for a one-dimensional oscillation problem by Rayleigh (1894) who studied in his *"Theory of Sound"* the case

$$F(v) = (a - bv^2)v; \qquad D(v) = 0 \tag{6.8}$$

with $b > 0$. Then the equation of motion has for $a < 0$ the only stationary state $v = 0$ and for $a > 0$ it possesses two stationary states

$$v = \pm v_0; \qquad v_0 = \sqrt{\frac{a}{b}} \tag{6.9}$$

The point $a = 0$ corresponds to a kinetic phase transition which possesses quite interesting properties (Klimontovich, 1982, 1986; Haken, 1983; Horsthemke & Levefer, 1984). Klimontovich (1982,1986) studied this system in much detail including a Langevin source with constant noise. Assuming $m = 1$ the Hamiltonian is $H = v^2/2$. We see that the dissipative force is fully determined by the Hamiltonian

$$F(v) = -(a - 2bH)v \tag{6.10}$$

Such systems are called "canonical dissipative". This rather interesting class of systems will be analyzed in more detail in the next section. The Fokker-Planck equation reads now

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial v}\left[(2bH - a)vP(v,t) + D_v\frac{\partial P(v,t)}{\partial v}\right] \tag{6.11}$$

This equation has the following solution which represents a stationary distribution function (Klimontovich, 1982, 1986)

$$f_0(v) = \rho(H) = C\exp\left[-\frac{aH - bH^2}{D_v}\right]. \tag{6.12}$$

For $a < 0$ this distribution is quite similar to a Maxwellian. For $a > 0$ the system is driven away from equilibrium. In this case the velocity distribution is bistable and has two maxima in the velocity space. The maximum of the energy distribution corresponds to

$$H_0 = \frac{v_0^2}{2} = \frac{a}{2b}; \qquad v_0^2 = \frac{a}{b}$$

This corresponds to a system of particles which move all either with velocity v_0 to the right or with $-v_0$ to the left. The picture is like a hydrodynamic flow to the right or to the left. Lateron we will discuss interesting biological applications to the movement of swarms (see Chapter 12). The theory given above may be easily generalized to self-oscillating systems of a special type, discussed briefly already in Section 2.4, which have the equation of motion (Klimontovich, 1982, 1986)

$$\frac{dv}{dt} + \omega_0^2 x = (a - bH)v + (2D_v)^{1/2}\xi(t) \tag{6.13}$$

Here the Hamiltonian is given by $(m = 1)$:

$$H = \frac{1}{2}v^2 + \frac{1}{2}\omega_0^2 x^2. \tag{6.14}$$

Again the friction force is determined by a Hamiltonian, corresponding to the so-called canonical-dissipative structure. Let us first discuss the stationary state for $D = 0$. An exact solution of the dynamic equations is

$$x(t) = (v_0/\omega_0) \sin(\omega_0 t + \delta); \qquad v(t) = v_0 \cos(\omega_0 t + \delta) \tag{6.15}$$

The stationarity requires

$$H = H_0 = v_0^2 = a/b. \tag{6.16}$$

This is a sustained oscillation with stationary amplitude $x_0 = v_0/\omega_0$. Due to the canonical-dissipative character we may find again an exact solution for the stationary Fokker-Planck equation, which is similar to eq. (6.12). We find

$$f_0(v) = \rho(H) = C \exp\left[-\frac{aH - bH^2/2}{D_v}\right]. \tag{6.17}$$

Here we have to observe the different expression for the Hamiltonian H and consequently also for the normalization C. For the passive case $a < 0$ we may neglect the nonlinearity putting $b = 0$ and find simply a Maxwellian.

$$f_0(v) = \rho(H) = C \exp\left[-\frac{-|a|H}{D_v}\right] \tag{6.18}$$

For $a = 0$ we observe in the deterministic system a bifurcation which leads to the auto-oscillating regime. The distribution function for the transition point reads:

$$f_0(v) = \rho(H) = C \exp\left[-\frac{bH^2}{D_v}\right] \tag{6.19}$$

We notice the large dispersion which is characteristic for all phase transitions. The first moments of this distribution are (Klimontovich, 1982, 1986)

$$< H > = \frac{2}{\sqrt{\pi}}\sqrt{\frac{D_v}{2b}}; \qquad < H^2 > = \frac{D_v}{b} \tag{6.20}$$

In the case of driven motion $a > 0$, that means for the regime of developed oscillations, the distribution reads

$$f_0(v) = \rho(H) = C \exp\left[-\frac{b(H - a/b)^2}{2D_v}\right] \tag{6.21}$$

where the constant follows again from normalization (Klimontovich, 1982, 1986).

$$C = \sqrt{\frac{2b}{\pi D}}\left[1 + \Phi\left(\frac{a}{\sqrt{2bD_v}}\right)\right]^{-1}.$$

Here $\Phi(x)$ is the standard error function. We can easily check that the curve of maximal probability has the shape of a crater. In the limit of small noise ($D_v \to 0$) the curve of maximal probability is exactly above the deterministic limit cycle. This is, of course, a necessary condition which any correct solution of the Fokker-Planck equation has to fulfill. Further we note, that the exponent $(H - a/b)^2$ correspond to the Lyapunov function of the system identified in Section 2.4. We found this way a model system which is exactly solvable in equilibrium and for any distance from equilibrium. Admittedly the force function which we used $F = (a - bH)v$ is not very realistic from the physical point of view, however it may be shown, that the more realistic Rayleigh force $F = (a - bv^2)v$ introduced for modeling sound oscillations as well as the van der Pol force $F = (a - bx^2)$ introduced for modeling electric oscillations may be converted in good approximation to our canonical-dissipative force $F = (a - bH)v$. This may be shown by using the procedure of phase-averaging (Klimontovich, 1982, 1986). We may use our model system as a good testing ground for more advanced methods of nonequilibrium theory. A special conclusion is, that the stationary distribution functions may depend not only on invariants as in our case H, but also on higher powers of the invariants, as in our case H^2.

6.2 Canonical-dissipative systems

As we have seen in the previous section, there exist systems, were the dissipative forces are determined by the Hamiltonian, which allows for exact solutions. Now we will generalize this concept and treat a whole class of solvable systems. This idea is mainly based on works of *Haken and Graham* (Haken, 1973, Graham, 1981). We will show that at least for this special class of far from equilibrium systems, the so-called canonical-dissipative systems, a general ensemble theory similar to Gibbs approach may be developed (Graham, 1981; Ebeling, 1981, 2000, 2002; Feistel and Ebeling, 1989). The theory of canonical-dissipative systems is the result of an extension of the statistical physics of Hamiltonian systems to a special type of dissipative systems where conservative and dissipative elements of the dynamics are both determined only by invariants of the mechanical motion. This theory is in close relation to the simple example of driven Brownian motion and auto-oscillating systems, presented in the first section of this Chapter. Later we will show a close relation to a recently developed theory of active Brownian particles (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000; Schweitzer et al., 2001; Schweitzer, 2003). The main ideas of the theory of active Brownian motion will be explained in Chapter 12.

We start the development of the theory of canonical-dissipative systems with a rather general study of the phase space dynamics of a driven many-particle system with f degrees of freedom $i = 1, ..., f$. Assuming that the Hamiltonian is given by $H(q_1...q_f p_1...p_f)$ the mechanical motion is given by Hamilton equations. The solutions are trajectories on the plane $H = E = const$. The constant energy $E = H(t = 0)$ is given by the initial conditions, which are (in certain limits) arbitrary. We construct now a canonical-dissipative system with the same Hamiltonian

(Haken 1973; Graham 1981; Ebeling, 2000; Schweitzer et al., 2001)

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - g(H)\frac{\partial H}{\partial p_i} \tag{6.22}$$

We will assume that the dissipation function $g(H)$ is nondecreasing. Equation (6.22) defines a canonical-dissipative system which does not conserve the energy. In regions of the phase space where $g(H)$ is positive, the energy decays and in regions where $g(H)$ is negative, the energy increases. The simplest possibility is constant friction $g(H) = \gamma_0 > 0$ which corresponds to a decay of the energy to the ground state. Of more interest is the case when the dissipative function has a root $g(E_0) = 0$ at a given energy E_0. Then the states with $H < E_0$ are supported with energy, and from states with $H > E_0$ energy is extracted. Therefore any given initial state with $H(0) < E_0$ will increase its energy up to reaching the shell $H(t) = E_0$ and any given initial state with $H(0) > E_0$ will decrease its energy up to the moment when the shell $H(t) = E_0$ is reached. Therefore $H = E_0$ is an attractor of the dynamics, any solution of eq.(6.22) converges to the surface $H = E_0$. On the surface $H = E_0$ itself the solution corresponds to a solution of the original Hamiltonian equations for $H = E_0$. The simplest dissipation function with the wanted properties is a linear function

$$g(H) = c(H - E_0) \tag{6.23}$$

The speed of the relaxation process is proportional to c^{-1}. The linear dissipative function (6.23) has found applications to Toda chains (Makarov et al., 1999). More general dissipative functions were considered in the theory of active Brownian motions (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000). We mention that all noninteracting systems $H = H(\boldsymbol{p}^2)$ with $g = g(\boldsymbol{p}^2)$ are canonical-dissipative. The attractor of the dissipative system (6.22) is located on the surface $H = E_0$. This does not mean that the full $(2f - 1)$-dimensional surface is the attractor of the system. Such a statement is correct only for the case $f = 1$, which has been considered in the last section, further this statement may be true also for systems which are ergodic on the surface $H = E_0$. In the general case the attractor may be any subset of lower dimension, possibly even a fractal structure.

Let us consider for example the case of one particle moving in an external field with radial symmetry

$$H = \frac{\mathbf{p^2}}{2m} + U(r); \qquad \boldsymbol{p} = m\boldsymbol{v}. \tag{6.24}$$

Then the equation of motion reads

$$\frac{d\mathbf{p}}{dt} = -\frac{\partial H}{\partial \mathbf{r}} - g(H)\mathbf{v}. \tag{6.25}$$

The corresponding equation for the angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ reads

$$\frac{d\boldsymbol{L}}{dt} = -\frac{1}{m}g(H)\boldsymbol{L}. \tag{6.26}$$

We see that on surfaces with $g(H) = 0$ obligatory $\mathbf{L} = \mathbf{L_0} = const$ holds. Of special interest are cases where this constant is different from zero. In other words, the system shows rotations. The concrete value of $\mathbf{L_0}$ may be obtained by explicit solutions of the equations of motion on the surface $H = E_0$.

A more general class of canonical-dissipative systems is obtained, if beside the Hamiltonian also other invariants of motion are introduced into the driving functions. Let us assume that the driving functions depend on $H = I_0$ and also on some other invariants of motion $I_0, I_1, I_2, ..., I_s$ for example

- $\mathbf{I}_1 = \mathbf{P}$ - total momentum of the system,

- $\mathbf{I}_2 = \mathbf{L}$ - total angular momentum of the system. etc.

For the equation of motion we postulate

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - \frac{\partial G(I_0, I_1, I_2, ...)}{\partial p_i}. \tag{6.27}$$

We include now an external white noise source restricting now our study to the case were the dynamics is determined by H. The Langevin equations read

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - g(H)\frac{\partial H}{\partial p_i} + (2D(H))^{1/2}\xi(t) \tag{6.28}$$

The essential assumption is, that noise and dissipation depend only on H. The corresponding Fokker-Planck equation reads

$$\frac{\partial \rho}{\partial t} + \sum \frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \sum \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \tag{6.29}$$

$$= \sum \frac{\partial}{\partial p_i}\left[g(H)\frac{\partial H}{\partial p_i}\rho + D(H)\frac{\partial \rho}{\partial p_i}\right] \tag{6.30}$$

An exact stationary solution is

$$\rho_0(q_1...q_f p_1...p_f) = Q^{-1}\exp\left(-\int_0^H dH'\frac{g(H')}{D(H')}\right) \tag{6.31}$$

The derivative of ρ_0 vanishes if $g(H = E_0) = 0$. This means the probability is maximal at the surface $H = E_0$.

For the special case of a linear dissipation function we find a stationary solution

$$\rho_0(q_1...q_f p_1...p_f) = Q^{-1}\exp\left(\frac{cH(2E_0 - H)}{2D}\right) = Q_1^{-1}\exp\left(\frac{-c(H - E_0)^2}{2D}\right). \tag{6.32}$$

The problem with these distributions is, that they might be formally exact but nevertheless lacking physical meaning. In particular, distributions of type (6.31) do not admit translational or rotational flows, since

$$\langle p_i \rangle = 0; \qquad \langle L_i \rangle = 0 \tag{6.33}$$

holds for symmetry reasons. Let us consider for example a mass point rotating in a central field on a plane. Then $H = E_0$ is a sphere in a 4-dimensional space. Since the angular momentum has only two possible directions (up or down), corresponding to right or left rotations, the system is unable to fill the whole surface $H = E_0$ but just a part of it, compatible with these two possibilities of left or right rotations. The easiest way to admit rotations is to include, as for the equilibrium case explained in Section 4.4., the invariant $\boldsymbol{\Omega} \cdot \boldsymbol{L}$ into the distribution

$$\rho_0(q_1...q_f p_1...p_f) = Z^{-1}(\Omega') \exp\left(-\int_0^H dH' \frac{g(H')}{D(H')} + \boldsymbol{\Omega}' \cdot \boldsymbol{L} \right) \tag{6.34}$$

This distribution admits rotations due to the different symmetry character. The mean value of the angular momentum is given by

$$\langle \boldsymbol{L} \rangle = \frac{\partial \ln Z(\boldsymbol{\Omega}')}{\partial \boldsymbol{\Omega}'}. \tag{6.35}$$

By replacing the mean value by the deterministic value $\boldsymbol{L}_0$

$$\boldsymbol{L}_0 = \frac{\partial \ln Z(\boldsymbol{\Omega}')}{\partial \boldsymbol{\Omega}'} \tag{6.36}$$

we may get a good approximate solution, reflecting the most important physical properties of our dynamical system. More general forms of the distribution will be discussed in Section 5.5. The existence of exact solutions for the probability distributions admits to derive the thermodynamic functions as the mean energy and the entropy. The system has further a Lyapunov functional K which is provided by the Kullback entropy which is a nonincreasing function

$$K[\rho, \rho_0] = \int dq_1...dq_f dp_1...dp_f \rho \log[\rho/\rho_0]. \tag{6.37}$$

This theorem governs the approach to the stationary state.

6.3   Microcanonical non-equilibrium ensembles

As shown above, canonical-dissipative forces drive the system to certain subspaces of the energy surface, where the total momentum or the angular momentum are fixed. In many cases the system is ergodic on these surfaces; this question has to be checked separately for any special case. Assuming that ergodicity (quasi-ergodicity) is given we may postulate that in the long run the measure of the trajectories is equally distributed on certain shells around the surfaces

$$H(q_1...q_f p_1...p_f) = E_0, \tag{6.38}$$

$$I_k(q_1...q_f p_1...p_f) = I_k, k = 2, 3, ..s. \tag{6.39}$$

The idea about the ergodicity of the trajectories leads us to microcanonical ensembles. There exist many examples of physical systems which are well described by microcanonical ensembles (Gross, 2001). Here we consider systems which are uniform in space but far from equilibrium. As examples may serve laser plasmas, homogeneous turbulent fluids and systems of active Brownian particles. These systems have in common, that they are driven by energy supply to far from equilibrium states. We construct now a special non-equilibrium ensemble which is characterized by a constant probability density on a energy shell

$$E_0 - \frac{1}{2}\delta E \le H(q_1...q_f p_1...p_f) \le E_0 + \frac{1}{2}\delta E. \tag{6.40}$$

This is a rather restrictive assumption, in particular it means that due to the symmetry of the system all mean fluxes are zero. The mean energy of the ensemble is fixed $\langle H \rangle = E_0 = U$. and the entropy is given by the volume of the energy shell according to Boltzmann's formula. Since our system is not in thermal equilibrium, not all thermodynamic relations, e.g.the relation between energy and temperature, are valid. The most typical properties of an equilibrium ensemble is, that the mean energy is proportional to the noise level T and that the mean quadratic deviation $\langle (\delta H)^2 \rangle$ is proportional to T^2. In the equilibrium all energy comes from the thermal fluctuations. In nonequilibrium the energy of the nonlinear excitations and the noise energy are decoupled. In other words, the energy $\langle H \rangle = U \simeq E_0$ is given mostly by the properties of the energy source and is nearly independent of the noise level which we will denote from now by D. On the other hand the energy fluctuations depend strongly on the noise strength D and are nearly independent on the energy of the excitations

$$\left(\delta E^2\right) = \left(\langle H^2 \rangle - \langle H \rangle^2\right) \simeq D. \tag{6.41}$$

We see immediately that the canonical distribution is not compatible with these properties. By constructing other exponential distribution functions from the maximum entropy principle we have to observe the correct behavior of the mean and the dispersion (Ebeling & Röpke, 2004). The most simple example of a distribution with the right properties is the Gaussian eq.(6.32). As an example may serve a nonequilibrium gas where all particles move with the same modulus of the velocity $\boldsymbol{v}_i = v_0^2$, a so-called isokinetic ensemble (Hoover, 2001). The direction of the velocities fluctuates stochastically. A physical system which behaves in such a way is a fluid in the state of uniform turbulence. Other examples are strongly excited laser plasmas and active Brownian particles.

In a generalization of the approach described above we assume that beside the energy also some other invariants of motion as e.g. the momentum or the angular momentum are conserved. Then the generalized microcanonical ensemble assumes that the probability density is constant on the shells around the prescribed invariants

$$I_k - \frac{1}{2}\delta I_k \le I_k(q_1...q_f p_1...p_f) \le I_k + \frac{1}{2}\delta I_k \tag{6.42}$$

for $k = 0, 1, ..., s$. This means that the density is concentrated on certain submanifolds of the energy shell $k = 0$. We note that the invariants are not necessarily smooth functions. Fluxes may be prescribed as far as they are expressed by invariants of motion, e.g a macroscopic flow may be prescribed by the total momentum $\boldsymbol{I}_1 = \boldsymbol{P}$. The entropy is given by the Boltzmann formula

$$S = k_B \log \Omega(I_0, I_1, ..., I_s). \tag{6.43}$$

where Ω expresses the volume of the manifold defined by the fixed invariants of motion.

6.4 Systems driven by energy depots

We started this Chapter with an example of a driven system far from equilibrium which goes back to to Klimontovich (1982, 1986, 1995). The simple Klimontovich system, which allows a full treatment, is a unification of the model of Brownian motion due to Einstein, Smoluchowski and Langevin with the model of (acoustic) oscillators driven by negative friction which originally is due to Rayleigh and Helmholtz. A "minus" of this nice model is it purely phenomenological character. We did not touch at all the question, where the forces, driving the system out of equilibrium, may come from. Let us start from a Langevin equation for a particle with coordinate $\boldsymbol{r}$ and velocity $\boldsymbol{v}$:

$$m\frac{d\boldsymbol{v}}{dt} + \nabla U(\boldsymbol{r}) = \boldsymbol{F}(\boldsymbol{v}) + m(2D_v)^{1/2}\boldsymbol{\xi}(t). \tag{6.44}$$

Now we will derive the dissipative force $\boldsymbol{F}(\boldsymbol{v})$ in a more physical way from energy depot models. There are many possibilities to couple a system to energy reservoirs. We will start with the treatment of two different variants. The first variant of the depot model (SET-model) developed in (Schweitzer et al., 1998, Ebeling et al., 1999) is based on the ansatz

$$\boldsymbol{F}(\boldsymbol{v}) = m\boldsymbol{v}(de - \gamma_0) \tag{6.45}$$

where e is the energy content of a depot and d a conversion parameter. The first term expresses an acceleration in the direction of $\boldsymbol{v}$. The second term $m\gamma_0\boldsymbol{v}$ is the usual passive friction, which by assumption is connected with the noise by an Einstein relation $D_v = \gamma_0 k_B T/m$. We assume further that the Brownian particles are able to take up energy with the rate q, which can be stored in the depot e. This internal energy can be converted into kinetic energy with a momentum dependent rate $d\boldsymbol{v}^2$, which results in the acceleration in the direction of movement. The internal energy dissipates with the rate ce, The balance of the depot energy then reads

$$\frac{de}{dt} = q - ce - de\boldsymbol{v}^2. \tag{6.46}$$

The energy balance of the particle follows by multiplying the Langevin equation with the velocity v, we get

$$\frac{dH}{dt} = dem\boldsymbol{v}^2 - m\gamma_0\boldsymbol{v}^2 + m\boldsymbol{v}\sqrt{2D_v} \cdot \boldsymbol{\xi}(t). \tag{6.47}$$

Assuming $q > 0$ and requiring that the internal energy depot relaxes fast compared to the motion of the particle we get in adiabatic approximation for the *depot model*

$$\boldsymbol{F} = m\boldsymbol{v}\left(\frac{dq}{c + dv^2} - \gamma_0\right) \tag{6.48}$$

For sufficiently large values of q and d the friction function may have a zero at

$$\boldsymbol{v}_0^2 = \frac{q}{\gamma_0} - \frac{c}{d} = \frac{c}{d}\zeta \tag{6.49}$$

$$\zeta = \frac{qd}{c\gamma_0} - 1$$

For positive values of the bifurcation parameters ζ and small velocities $|\boldsymbol{v}| < v_0$, we observe input of free energy, the system is driven (self-propelling). Another convenient way of writing the friction function is

$$\gamma(v^2) = \gamma_0(1 - \frac{\delta}{1 + v^2/v_1^2}) \tag{6.50}$$

with $v_1^2 = c/d$ and $\delta = \zeta + 1$. This friction force was first studied in (Schweitzer et al., 1998; Ebeling et al., 1999; Erdmann et al., 2000). The parameter $v_1 > 0$ is connected to internal dissipation and δ controls the conversion of the energy taken up from the external field into kinetic energy. Actually, the parameter δ is now the essential bifurcation parameter of this model. The parameter value $\delta = 0$ corresponds to equilibrium, the region $0 < \delta < 1$ stands for nonlinear passive friction and $\delta > 1$ corresponds to active friction. The value of the transition (bifurcation) from one to the other regime is $\delta = 1$. For the passive regime $0 < \delta < 1$ the friction function has one zero point at $v = 0$ which is the only attractor of the deterministic motion. In Fig. (6.1) we represented the velocity-dependent friction for different values of driving. Without noise all particles come to rest at $v = 0$. For $\zeta > 1$ the point $v = 0$ becomes
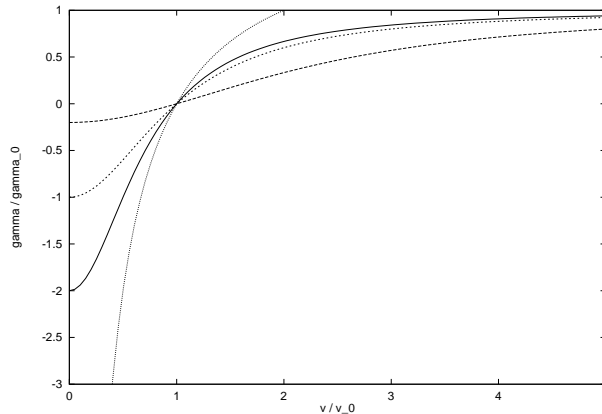

Figure 6.1: Friction function for several values of the driving strength.

unstable but we have now two additional zeros at

$$v = v_0 = \pm v_1 \sqrt{\delta - 1} \tag{6.51}$$

These two velocities are the new attractors of the free deterministic motion if $\delta > 1$. In Fig. 6.2 we have plotted the friction force for the two values $\delta = 0$ (equilibrium) and $\delta = 2$ (strong driving). The figure includes the representation of a useful piecewise linear approximation of
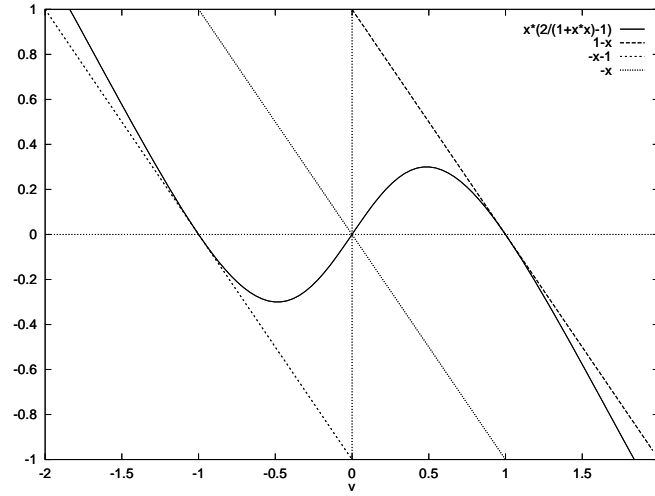

Figure 6.2: Dissipative force for the parameter values $\delta = 0$ (equilibrium) and $\delta = 2$ (strong driving) and a piecewise linear approximation for $\delta = 2$.

the friction force for $\delta > 1$ which reads

$$\boldsymbol{F} = -m\gamma_1 \boldsymbol{v} \left[1 - \frac{v_0}{|v|} \right], \tag{6.52}$$

$$\gamma_1 = 2\gamma_0 \frac{\delta - 1}{\delta}$$

This is a linear approximation to the friction force near to the two stable velocities $v = \pm v_0$. We see also that between the zero points the force function may be well approximated by a cubic law

$$\boldsymbol{F} = m\boldsymbol{v} \left[a - bv^2 \right] \tag{6.53}$$

with $v_0^2 = a/b$. This simple law was introduced already in the 19th century by Lord Rayleigh in his *"Theory of sound"* (Rayleigh, 1893). One-dimensional stochastic systems with a friction function corresponding to Rayleigh's law were discussed in detail by Klimontovich (1983, 1995). The piecewise linear friction function introduced above as an approximation is similar to the

friction law found empirically by Schienbein and Gruler from experiments with cells (Schienbein & Gruler, 1993; Schienbein et al., 1994). The Schienbein-Gruler function reads

$$\text{F} = -m\gamma_0 \boldsymbol{v} \left[1 - \frac{v_0}{|v|} \right]. \tag{6.54}$$

The asymptotics of the depot model (SET-model) is in agreement with the Schienbein-Gruler model; in both cases we have the asymptotics $-\gamma_0 \boldsymbol{v}$. In the zero point v_0 the derivative in the zero point is in the SET-model $-\gamma_1$ and in the Schienbein Gruler law it is fixed by γ_0.

Let us come now to the question of the distribution functions. The systems of active Brownian particles introduced above are canonical dissipative systems in the sense discussed in the previous section. Therefore the distribution function can be given exactly. On order to prove this we write

$$\boldsymbol{F} = -m\boldsymbol{v}\gamma(v^2) \tag{6.55}$$

Since v^2 is proportional to the kinetic energy - and there is no potential energy so far - this system is indeed canonical-dissipative. Based on the canonical-dissipative character we find in the general case the distribution function

$$\rho = C \exp\left(-\frac{m}{2D_v} \int \gamma(v^2) dv^2 \right). \tag{6.56}$$

Let us discuss now more concrete cases. The distribution for the depot model (SET- model) reads:

$$\rho_0(v_x, v_y) = C \exp\left[-\frac{mv^2}{2kT} + \frac{q}{2D_v} \log\left(1 + \frac{d}{c}v^2 \right) \right]. \tag{6.57}$$

Approximately this may be written as

$$\rho_0(v_x, v_y) = C \exp\left[-\frac{qd^2}{4D_v c^2}(v^2 - v_0^2)^2 \right]. \tag{6.58}$$

For piecewise linear force laws, including the Schienbein-Gruler law, the distribution is of particular simplicity

$$\rho(v_x, v_y) = C \exp\left(-\frac{\gamma_1}{2D_v}(|\boldsymbol{v}| - v_0)^2 \right) \tag{6.59}$$

The piecewise linear force law may be used as an approximation for arbitrary friction laws of type (6.55). Since the modulus of $\boldsymbol{v}^2$ is most time around the value v_0^2 the linearization is well justified. Due to the simplicity of piecewise linear friction laws we are able to find also several more general solutions. In particular the *mean square displacement* may be calculated (Schienbein et al., 1994; Mikhailov & Meinköhn, 1997; Erdmann et al., 2000)

$$\langle (\boldsymbol{r}(t) - \boldsymbol{r}(0))^2 \rangle = \frac{2v_0^4}{D_v}t + \frac{v_0^6}{D_v^2}\left[\exp\left(-\frac{2D_v t}{v_0^2} \right) - 1 \right]. \tag{6.60}$$
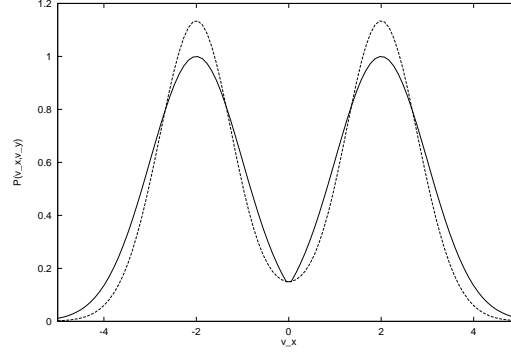
Figure 6.3:

Distribution function of the velocity for the depot model (dashed line) and for the piecewise linear approximation (full line). (Parameters: $D_v = \gamma_0 = c = d = 1, q = 5, v_0 = 2$.)

The analytical expressions for the stationary velocity distribution and for the mean squared displacement are in good agreement with computer simulations (Schweitzer et al., 2001) and with measurements on the active movements of granulocytes (Schienbein & Gruler, 1993; Schienbein et al., 1994). We notice also the close relation of this theory to systems with isokinetic thermostats (Hoover et al., 1987; Hoover, 2001). Driving by velocity-dependent dissipative forces may have similar effects as driving by isokinetic thermostats as will be shown in the next section. In the adiabatic approximation all the models discussed above have similar properties, in particular they are of canonical-dissipative form.

Summarizing the results of this and the previous sections we underline that these studies were limited to a rather special type of nonequilibrium systems which are pumped from external sources with free energy. We started from the Hamiltonian theory of mechanical systems and constructed forces to drive them away from equilibrium. Then in order to extend the known methods of statistical physics for conservative systems to dissipative systems we developed a general theory of canonical-dissipative systems. Special canonical-dissipative system were constructed, which solution converges to the solution of the conservative system with given energy, or other prescribed invariants of motion. In this way we were able to generate nonequilibrium states characterized by certain prescribed invariants of mechanical motion. We postulated special distributions which are analogues of the microcanonical ensemble in equilibrium. Further we found solutions of the Fokker-Planck equation which may be considered as analogues of the canonical equilibrium ensembles. We proposed to call these distributions canonical-dissipative ensembles. By the help of the explicit nonequilibrium solutions we were able to construct for canonical-dissipative systems a complete statistical thermodynamics including an evolution criterion for the nonequilibrium.

In Chapter 12 we will study applications of the theory to problems of active Brownian motion.

We will show that this class on systems is of interest for modeling biological motion (Gruler & Schienbein, 1993, Schweitzer, 2002) and traffic (Helbing, 1997, 2001). Finally we want to say, that canonical-dissipative systems are a rather artificial class of models. In reality, canonical-dissipative systems, strictly according to their definition, do not exist. However there are many complex systems which have several properties in common with canonical-dissipative systems as

- the mechanical character of the motion, i.e. the existence of space and momentum, of quasi-Newtonian dynamics etc.,

- the support of the dynamics with free energy from internal or external reservoirs and the existence of mechanisms which convert the reservoir energy into acceleration.

If so, then the question arises, how systems near to having canonical-dissipative character can be treated by some kind of perturbation theory (see e.g. Haken, 1973; Ebeling, 1981).

6.5 Systems of particles coupled to Nose-Hoover thermostats

The nonequilibrium systems which we considered so far, were driven by negative friction, the stochastic effects were generated by an embedding into a thermal reservoir. This thermostat was assumed to be in equilibrium, what determined the passive friction and the noise. In connection with molecular-dynamical simulations, Nose' (1991) and Hoover (1988, 1998, 1999, 2001) developed a completely different class of thermostats, which found many applications (Hoover & Posch, 1996, Klages et al., 1999; Rateitschak et al., 2000). Because of the great interest in these systems, we will discuss now this new kind of imbedding.

The equations of motion for a Nose-Hoover thermostated particle on a plane confined in a parabolic well read (Hoover, 1998; 2001)

$$\frac{d}{dt}\boldsymbol{r} = \boldsymbol{v}\,;\ \ \frac{d}{dt}\boldsymbol{v} = -\gamma(t)\boldsymbol{v} - a\boldsymbol{r} \tag{6.61}$$

here γ is a variable friction

$$\frac{d}{dt}\gamma = \frac{1}{\tau^2}\left(\frac{v^2}{2T} - 1\right) \tag{6.62}$$

In the following we will use instead of the temperature T of the thermostat a characteristic velocity $v_0^2 = 2T$. By multiplication with v we get the energy balance

$$\frac{d}{dt}\left(\frac{v^2}{2} + \frac{ar^2}{2}\right) = -\gamma v^2 \tag{6.63}$$

The solutions for v^2 and γ are typically periodic functions. Let us now first consider the case $a = 0$. In Fig. 6.4 we have shown periodic trajectories in the plane v^2 vs. γ. The shape of the
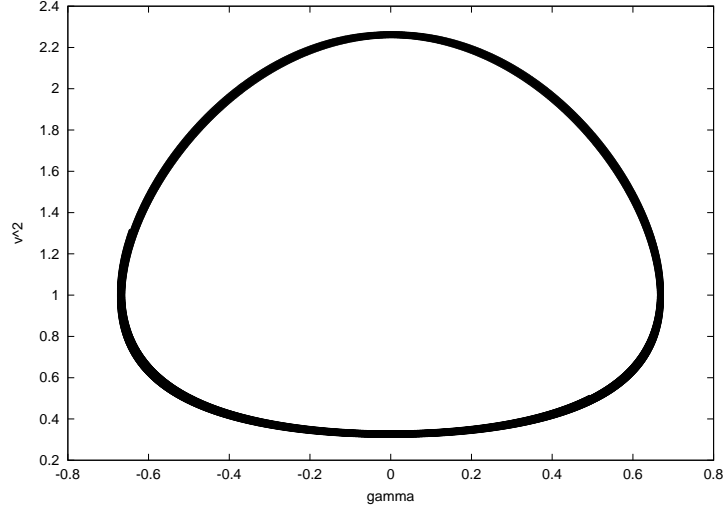

Figure 6.4: Typical trajectories of free particles with a Nose-Hoover thermostat on the plane v^2 against γ.

trajectories is a hint to the existence of invariants of motion. By subtracting both equations and using the relation

$$\gamma = -\frac{d}{2dt} \log(v^2) \tag{6.64}$$

we find the following invariant of motion

$$\frac{d}{dt} \left(\frac{v^2}{2} - \frac{v_0^2}{2} \log \frac{v^2}{v_0^2} + \frac{\tau^2}{2}\gamma^2 \right) = 0 \tag{6.65}$$

Therefore the trajectories are located on the surface

$$I_0 = \frac{v^2}{2} - \frac{v_0^2}{2} \log \frac{v^2}{v_0^2} + \frac{v_0^2}{2}\tau^2\gamma^2 = const. \tag{6.66}$$

The invariant of motion I_0 has the dimension of an energy (in our units $m = 1$). In Fig. 6.5 we have demonstrated the invariant I_0 and $v^2(t)$ as functions of time. There seems to be a relation between I_0 and Dettmann's Hamiltonian (Hoover, 2001). In Fig. 6.6 the invariant is represented in the plane v^2 against γ for a noisy integration. The distribution function for a canonical ensemble is given by

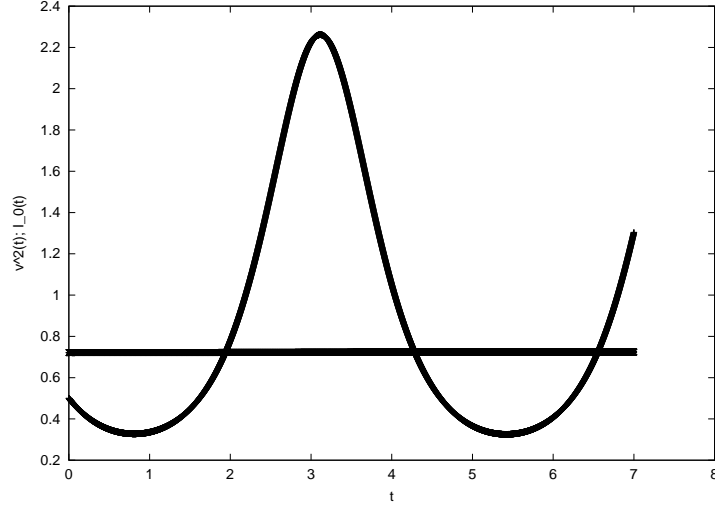$$f_0(\boldsymbol{v}) = C \exp\left(-\beta I_0(v, \gamma)\right). \tag{6.67}$$

Figure 6.5: Free particles in the NH-thermostat. We show the time dependence of $v^2(t)$ and the invariant I_0 according to a numerical integration.

In an approximation where $\beta v_0^2 \ll 1$ we find

$$f_0(\boldsymbol{v}, \gamma) = C \exp\left(-\beta \frac{v^2}{2} - \beta \tau^2 \frac{\gamma^2}{2}\right). \tag{6.68}$$

In the opposite case where $\beta v_0^2 \gg 1$ we get

$$f_0(\boldsymbol{v}, \gamma) = C \exp\left(-\beta \frac{1}{4v_0^2}(v^2 - v_0^2)^2 - \beta \tau^2 \frac{\gamma^2}{2}\right). \tag{6.69}$$

Finally we consider also the case of many particle $i = 1, 2, ..., N$ driven by thermostats through a time-dependent friction function

$$\frac{d}{dt}\boldsymbol{r}_i = \boldsymbol{v}_i \, ; \;\; \frac{d}{dt}\boldsymbol{v}_i = -\gamma_i(t)\boldsymbol{v}_i - a\boldsymbol{r}_i + \sqrt{2D}\xi_i(t) \tag{6.70}$$

In this case we may distinguish between two types of thermostats:
(i) individual thermostats defined by

$$\frac{d}{dt}\gamma_i = \frac{1}{\tau^2}\left(\frac{v_i^2}{2T} - 1\right) \tag{6.71}$$

(ii) collective thermostats with the same friction for all particles

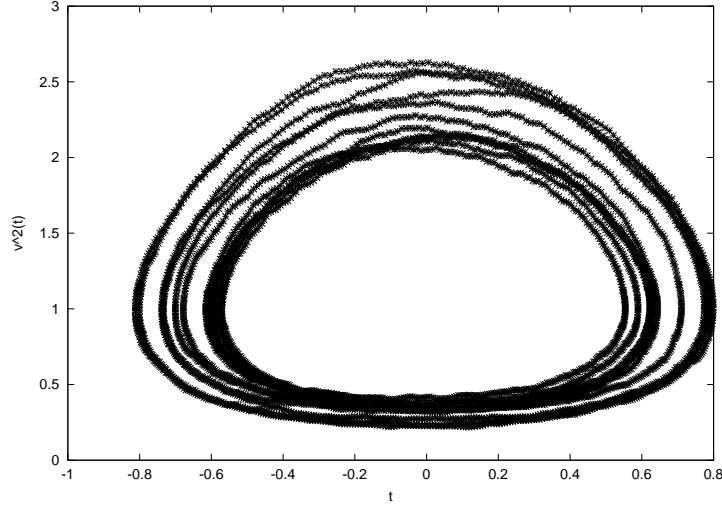$$\frac{d}{dt}\gamma = \frac{1}{\tau^2}\left(\frac{\sum v_i^2}{2NT} - 1\right) \tag{6.72}$$

Figure 6.6: The invariant of free particles in the NH-thermostat from a noisy integration.

Collective of thermostats (case (ii)) correspond in the case $\beta v_0^2 \gg 1$ approximately to a quasi-microcanonical ensemble in the dimension $d = 3N$. As shown by Klages et al. (1999) the distribution functions of this system may show central dips depending on the dimension d. We conclude this section by discussing the relations between Nose-Hoover thermostats and the depot models discussed in the previous section. We introduce first a generalized depot model with dissipative forces $\boldsymbol{F}$ in the following form:

$$\boldsymbol{F}(e, \boldsymbol{v}) = \boldsymbol{v}(de^n - \gamma_0). \tag{6.73}$$

where e is the energy content of a depot and d is a conversion parameter. The first term expresses an acceleration in the direction of $\boldsymbol{v}$. The second term $\gamma_0 \boldsymbol{v}$ is the usual passive friction, which by assumption is connected with the noise by an Einstein relation $D = \gamma_0 kT/m$. We assume further that the Brownian particles are able to take up energy, which can be stored in the depot e. This internal energy can be converted into kinetic energy with a momentum dependent rate $de^n v^2$, which results in the acceleration in the direction of movement. The exponent n is free so far. The dissipative flow of energy into the mechanical systems is

$$\boldsymbol{v} \cdot \boldsymbol{F} = \boldsymbol{v}^2(de^n - \gamma_0). \tag{6.74}$$

If this energy flow comes from a depot with content e then we have the depot dynamics

$$\frac{de}{dt} = s(e) - de^n \boldsymbol{v}^2. \tag{6.75}$$

Here $s(e)$ is a function describing the support of the depot from an outside source. Now we specify the model: Asuming $n = 1$ and $s(e) = q - ce$ we come back to the depot model studied

in section 5.4. In order to find a Nose-Hoover-type dynamics we assume the exponent is $n = 1/2$ and postulate further the following balance of the depot (Ebeling & Röpke, 2003)

$$\frac{de}{dt} = q\sqrt{e} - ce - d\boldsymbol{v}^2\sqrt{e}. \tag{6.76}$$

Within this model we get in adiabatic approximation assuming $q > 0$ and requiring that the internal energy depot relaxes fast compared to the motion of the particle

$$\boldsymbol{F} = \boldsymbol{v}\left(\frac{d}{c}(q - dv^2) - \gamma_0\right). \tag{6.77}$$

Now, under the condition $((qd/c) - \gamma_0) > 0$, a root $v_0 > 0$ exists and we get a cubic law which corresponds to the Rayleigh friction law. We reformulate now the model in order to show the relation to NH-thermostats. Introducing a time-dependent friction variable $\gamma = \gamma_0 - d\sqrt{e}$ we find the "dissipative force"

$$\boldsymbol{F} = -\gamma(t)\boldsymbol{v}. \tag{6.78}$$

The friction variable satisfies the dynamic equation

$$\frac{d\gamma}{dt} = \frac{d}{2}\left(dv^2 - \frac{c}{d}\gamma - q + \frac{c}{d}\gamma_0\right). \tag{6.79}$$

By introducing here the new variables

$$v_0^2 = \frac{q}{d} - \frac{c\gamma_0}{d^2} \tag{6.80}$$

and

$$\tau^2 = \frac{2}{d^2 v_0^2}, \qquad \xi = \frac{c}{2} \tag{6.81}$$

we get the dynamics

$$\frac{d\gamma}{dt} = \frac{1}{\tau^2}\left(\frac{v^2}{v_0^2} - 1\right) - \xi\gamma, \tag{6.82}$$

where ξ is a dissipative constant. Assuming a special time evolution for ξ, we arrive at a dynamics discussed in section 7.10.3 of Hoover's book (Hoover, 2001). In the limit $\xi = 0$, i.e. $c = 0$ our system reduces to a conservative Nose-Hoover dynamics (Hoover, 1988, 1998, 2001; Klages et al., 1999). In the case $\xi = const > 0$ we find a dissipative Nose-Hoover dynamics. The corresponding Langevin equation contains a stochastic force. In order to simplify we assume that only the passive friction generates noise

$$D = \gamma_0 kT \tag{6.83}$$

$$\langle \xi_i(t) \rangle = 0\,; \;\; \langle \xi_i(t)\xi_j(t') \rangle = \delta(t - t')\delta_{ij} \tag{6.84}$$

In the simplest case of force-free particles the kinetic energy is a conserved quantity: $v^2 = const$. This means, the system is canonical-dissipative. Consequently we are able to find exact solutions for the probability distribution following sections 5.3-5.4. For the dissipative Nose-Hoover dynamics we get the stationary distribution

$$f_0(v_1, v_2) = C \exp\left[-\alpha(v^2 - v_0^2)^2\right] \tag{6.85}$$

with $\alpha = d/(4cD)$. We notice the close relation to Lorentz gas distributions (Klages et al.,1999; Rateitschak et al. , 2000). In conclusion we may say, that driving by velocity-dependent dissipative forces may have similar effects as driving by isokinetic thermostats.

6.6   Nonequilibrium distributions from information-theoretical methods

In this section we will show, how non-equilibrium distribution functions may be constructed by means of the information-theoretical methods which were introduced in section 4.4. This method which basically was developed by Gibbs and Jaynes (Jaynes, 1957; 1985). was further developed and applied to nonequilibrium situations by Zubarev (Subarev, 1976; Zubarev et al., 1996, 1997)). This information-theoretical method is of phenomenological character and connected with the maximum entropy approach. There is no reason to restrict the method to the equilibrium case. As stated by Jaynes (1957, 1985) the method should work under much more general conditions. While in equilibrium we prescribe certain invariants of motion as e.g. energy, particle numbers etc. (see Section 4.4.) we have to look in nonequilibrium for more general observables. As we shall see, under non-equilibrium conditions, we should consider also macroscopic constraints due to the boundary conditions, as e.g. prescribed flows, angular momenta etc.. We consider quantities which may be represented as averages over the distribution and are prescribed in average by the conditions. This does not mean that these quantities are fixed, only the averages are prescribed and fluctuations around the means which are described by the distribution are possible. Then one constructs distribution functions which are compatible with the given averages. The free parameters in distribution function are found by maximizing the entropy of the distributions.

In the following we will pay special attention to the construction of non-equilibrium ensembles for systems with rotational modes, by using the Zubarev-formalism (Subarev, 1976; Zubarev, Morozov and Röpke, 1996, 1997). We will show in detail how the distributions are constructed if the angular integrals of motion are prescribed. Let us start now to explain the Jaynes-Zubarev approach to non-equilibrium systems. We consider an $N-$ particle system with the Hamiltonian:

$$H_S = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} V(\boldsymbol{r}_i - \boldsymbol{r}_j) . \tag{6.86}$$

Including an embedding in surroundings, a heat bath, we have two additional terms in the total Hamiltonian:

$$H_{total} = H_S + H_B + H_{SB} \tag{6.87}$$

here the bath is modeled by $H_B = H_B(Q, P)$, and the coupling by $H_{SB} = \sum_i^N V(\boldsymbol{r}_i, Q)$. Special cases are the isolated system with $H_{SB} = 0$ and external fields $V^{\text{ext}}(\boldsymbol{r}_i)$ modeling traps.

Let us discuss now the form of the distribution functions. In non-equilibrium, in general, the linear "ansatz" used in the previous Chapter (4.54) is no more sufficient, since the means and the dispersion may be independent variables. In order to admit such situations we have to use quadratic function in the exponent of the distribution function. Let us assume that the mean values of the observables A_k and A_k^2 are given. In order to find the probability density under the constraints

$$A_k' = \langle A_k \rangle = \int dq dp A_k(q, p) \rho(q, p) \tag{6.88}$$

$$A_k'' = \langle A_k^2 \rangle = \int dq dp A_k^2(q, p) \rho(q, p) \tag{6.89}$$

we maximize the information entropy

$$\mathcal{H} = -\int dq dp \rho(q, p) \ln \rho(q, p) \tag{6.90}$$

under the given constraints. We define two m-component vectors $\lambda' = [\lambda_1', ..., \lambda_m']$ and $\lambda'' = [\lambda_1'', ..., \lambda_m'']$ of Lagrange-multipliers. Then the probability density that agrees with the given data $\mathbf{A}'$ follows from

$$\delta[\mathcal{H} + \sum_k \lambda_k'(A_k' - \int dq dp A_k(q, p) \rho(q, p)) + \sum_k \lambda_k''(A_k'' - \int dq dp A_k^2(q, p) \rho(q, p))] = 0 \tag{6.91}$$

This leads to

$$\rho(q, p) = Z^{-1} \exp[-\sum_k (\lambda_k' A_k(q, p) + \lambda_k'' A_k^2(q, p)], \tag{6.92}$$

where the normalization factor, the so-called partition function, is now given by

$$Z(\lambda_1, ..., \lambda_m) = \int dq dp \exp[-\sum_k (\lambda_k' A_k(q, p) + \lambda_k'' A_k^2(q, p))]. \tag{6.93}$$

The choice of the parameters should reflect the conditions (6.88) and (6.89).

The choice of the observables A_k describing the physical problem is not clear from the beginning. Candidates are the invariants of the dynamics and quantities which are prescribed by the boundary conditions. Among the invariant quantities the angular momentum is of special interest.

We will consider now this class of observables in more detail. The interest in a theory of rotational systems is due to the important role of rotations in nature. For example we mention

the typical rotations of astrophysical objects as stars and planets, in macroscopic, mesoscopic and in atomic systems. In general one can say that most confined or selfconfined physical systems show rotational modes. In recent times finite Coulomb systems as quantum dots are in the center of interest (Bonitz et al., 2002; Dunkel et al., 2004).

In our context the $N-$ particle angular momentum is given as the sum of the momenta of the particles:

$$\boldsymbol{L}_N = \sum_i^N \boldsymbol{L}_i, \quad \boldsymbol{L}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i \ . \tag{6.94}$$

Further $\boldsymbol{L}_N^2$ and higher powers of the angular momenta sometimes are of interest (see e.g. the theory of atoms and molecules). The time evolution of the angular momentum is given by:

$$\frac{d}{dt}\boldsymbol{L}_N = \frac{i}{\hbar}[H, \boldsymbol{L}_N] = \frac{i}{\hbar}[H_{SB}, \boldsymbol{L}_N] \ . \tag{6.95}$$

We will assume central forces, so that any change of the angular momentum is due to the "bath". If the coupling H_{SB} is absent or has rotational symmetry then the total angular momentum is a conserved quantity. Alternatively we may prescribe the angular momentum by boundary conditions. The total angular momentum $\boldsymbol{L}_N$ is a conserved quantity, if the coupling H_{SB} is absent or has rotational symmetry. Alternatively we may prescribe it by boundary conditions. Let us assume that the average

$$\langle \boldsymbol{L}_N^n \rangle = \int d\Gamma \rho \boldsymbol{L}_N^n = const \tag{6.96}$$

for any given n is fixed. Then, we will postulate, that the distribution is a function of H_S and of $\boldsymbol{L}_N$

$$\rho = \rho(H_S, N, \boldsymbol{L}_N) \ . \tag{6.97}$$

The concrete form of the distribution is assumed to be determined by the expectation values. This may be a canonical distribution, but also any other forms of functional dependence are possible. Two cases are of special interest:

1) For rotating bodies of N particles which are only weakly coupled to an external heat bath and which otherwise are in internal equilibrium, the distribution is of particular simplicity. Assuming that conserved quantities H_N, N and $\boldsymbol{L}_N$ are the observables and that the corresponding Lagrange parameters are β, μ and $\boldsymbol{\omega}$, we find according to Section 4.4. an extended canonical Gibbs distribution (Landau & Lifshits, 1990).

$$\rho_{\text{eq}} = \frac{1}{Z_{\text{eq}}} \exp\left[-\beta(H_S - \mu N - \boldsymbol{\omega} \cdot \boldsymbol{L}_N)\right]. \tag{6.98}$$

here $\boldsymbol{\omega}$ is the angular velocity.

2) If the torque due to the surrounding bath is weak, then $\boldsymbol{L}_N$ is nearly conserved, it is a long-living mode of the system. In particular this is the case if the cluster and the surrounding have

nearly spherical symmetry. Then $\boldsymbol{L}_N$, $\boldsymbol{L}_N^2$, etc. are quasi-conserved and should be included in the relevant distribution ρ_{rel} (Zubarev et al., 1996, 1997; Ebeling & Röpke, 2004).

We may assume that several $n-$ order moments of the angular momentum are given at time t as e.g.

$$\langle L_N \rangle^t = \int d\Gamma \cdot \rho_{\text{rel}}(t) L_N,$$

$$\langle L_N^2 \rangle^t = \int d\Gamma \cdot \rho_{\text{rel}}(t) L_N^2. \tag{6.99}$$

We assume further that the relevant distribution ρ_{rel} is again a generalized Gibbs distribution but including higher momenta

$$\rho_{\text{rel}}(t) = \frac{1}{Z_{\text{rel}}(t)} \exp\left[-\beta\left(H_S - \mu N - \sum_n \boldsymbol{\Omega}_n(t) \boldsymbol{L}_N^n\right)\right] \tag{6.100}$$

In this distribution in addition to β, μ, the free parameters $\boldsymbol{\Omega}_n$ appear, which characterize nonequilibrium quantities. The following step according to Jaynes-Zubarev is to maximize the Gibbs entropy

$$S = \int d\Gamma \rho_{rel} \cdot \ln \rho_{rel} \tag{6.101}$$

under the given constraints (6.96). In this procedure the new parameters appear as the Lagrange multipliers $\boldsymbol{\omega}_{(n)}(t)$ and may be determined by the prescribed averages (6.96) as shown in detail e.g. in (Jaynes, 1957; Subarev, 1976; Zubarev et al., 1996). Of special importance for our problems is the case $n = 2$, i.e. the square of the angular momentum is given.

If the torque is weak, then the relaxation time of the angular momenta is quite long. An estimate of the relaxation time may be found also by linear response theory, which yields the expression (Zubarev et al.,1996)

$$\tau_L \propto \int_0^\infty dt \, \langle \left(\frac{d\boldsymbol{L}_N}{dt}\right)_t \left(\frac{d\boldsymbol{L}_N}{dt}\right)_{t=0} \rangle \, ,$$

The equilibrium correlation function may be evaluated by simulations or by analytical methods like perturbation expansions.

Among the quantities which may be prescribed by the surrounding, the kinetic energy is of special interest. Due to specific boundary conditions in some situations the individual kinetic energies are prescribed up to certain accuracy. For example, the interaction with a laser beam or with a surrounding plasma may fix the kinetic energies of the individual particles T_i around some value given by the laser intensity

$$T_i = \frac{m_i}{2} \boldsymbol{v}_i^2 \simeq T_0 \, .$$

In a recent papers Trigger and Zagorodny have shown that the charged grains in a dusty plasma have a velocity distribution which is peaked around a characteristic velocity (kinetic energy) of

the grains (Trigger and Zagorodny, 2002, 2003; Trigger, 2003).
As already mentioned, sometimes often the experimental conditions are such that the particles are driven to to a prescribed kinetic energy

$$\boldsymbol{v}_i^2(t) \rightarrow v_0^2$$

An example are charged grains in dusty plasmas (Trigger & Zagorodny, 2002, 2003, Trigger, 2003) or Coulomb clusters driven by a strong laser field. Due to the interaction with the surrounding, in the examples the "bath" is given by the plasma ions or the radiation field, the particles are accelerated to certain kinetic energy. In th is case we postulate that the distribution is of the following form

$$\rho_N(\boldsymbol{v}_1, ..., \boldsymbol{v}_N) = \Pi_{i=1}^N \tag{6.102}$$
$$\exp\left[-\alpha_v(\boldsymbol{v}_i^2 - v_0^2)^2\right]. \tag{6.103}$$

According to this distribution the most probable squared velocities (kinetic energies) are at the values v_0^2. Here α_v is an appropriate parameter characterizing the dispersion. We denote this type of ensemble "isokinetic ensemble". This notation is borrowed from molecular dynamics, where Gaussian isokinetic ensembles play a big role (Hoover, 1988, 1998, 1999; Rateitschak et al., 2000).
A generalization are conditions fixing the individual energies H_i of the particles on the given value H_0. This leads to the Gaussian distributions

$$\rho_N(r_1, ...r_N, v_1, ..., v_N) = \Pi_{i=1}^N \tag{6.104}$$
$$\exp\left[-\alpha_H(H_i - H_0)^2\right] \tag{6.105}$$

In radially symmetric systems the driving to v_0^2 or H_0 implies for a special class of systems (an example will be given below) that $\boldsymbol{L}_i$ is also fixed to certain L_{i0}. This is due to internal connections between the invariants of motion. The existence of rotations means, that the symmetry with respect to all directions in space is broken, i.e correspondingly the distribution functions should be modified. Therefore we will consider also the distributions

$$\rho_N(L_1, ..., L_N) = \Pi_{i=1}^N \exp\left[-\alpha_L(\boldsymbol{L}_i - L_{i0})^2\right] \tag{6.106}$$

A different 'ansatz' is based on the invariant $H - \boldsymbol{\Omega} \cdot \boldsymbol{L}$ which is a kind of internal Hamiltonian and reads

$$\rho_0(q_1...q_f p_1...p_f) = Z^{-1}(\Omega) \tag{6.107}$$
$$\exp\left(-\alpha_1(H - E_0)^2 - \alpha_2(H - \boldsymbol{\Omega} \cdot \boldsymbol{L})\right). \tag{6.108}$$

This way we may prescribe the most probable value of the total energy and of the internal energy separately by the choice of α_1, α_2.

More general forms of the distributions are Gaussian distributions centered around the prescribed invariants of motion

$$\rho_0(q_1...q_f p_1...p_f) = const.\Pi_{k=0}^s \tag{6.109}$$

$$\exp\left(-c_k \frac{(I_k(q_1...q_f, p_1...p_f) - I_k)^2)}{2D}\right). \tag{6.110}$$

However as we have shown above, there is no guaranty that the distributions constructed in this way already have the correct physical symmetry. This has to be checked in every concrete case. In the limit of very strong driving the probability reduces to a kind of microcanonical ensemble corresponding to the shell defined by $I_0, I_1, ..., I_s$ with a constant probability density on the shell. Let us discuss now in brief the physical meaning and symmetry properties of probability distributions which express prescribed angular momenta. Where is the probability
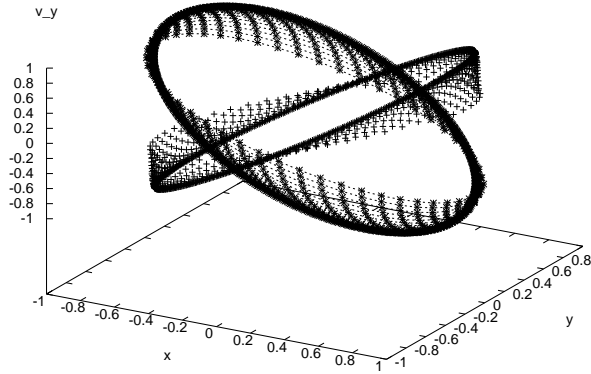

Figure 6.7:
Typical distribution of a rotating 2-d particle with fixed angular momentum $\boldsymbol{L}^2 = L_0^2$. The two possible values of the angular momentum select two tires on the sphere $H = const..$ We see a projection of the 4-dimensional phase on the $x - y - v_y-$ space.

concentrated in the phase space? We consider as a simple case of a particle rotating on a 2-dimensional plane, i.e. we have a 4-dimensional phase space (a physical realization was considered already in Section 5.1 and will be studied in more detail in Chapter 12). Then fixation of the most probable value of the total energy $H = E_0$ defines the surface of a sphere (or a cylinder if the kinetic energy is prescribed) in the 4-dimensional space:

$$\frac{m}{2}(v_1^2 + v_2^2) + \frac{m}{2}\omega_0^2(x_1^2 + x_2^2) = E_0$$

In order to characterize the two rotating states we introduce two non-negative invariants of motion

$$J_+ = H - \omega_0 L = \frac{m}{2}(v_1 + \omega_0 x_2)^2 + \frac{m}{2}(v_2 - \omega_0 x_1)^2 \tag{6.111}$$

and

$$J_- = H + \omega_0 L = \frac{m}{2}(v_1 - \omega_0 x_2)^2 + \frac{m}{2}(v_2 + \omega_0 x_1)^2. \tag{6.112}$$

The condition $J_+ = 0$ characterizes rotations with positive angular momentum ($L \simeq H_0/\omega_0$) and the condition $J_- = 0$ characterizes rotations with negative angular momentum ($L \simeq -H_0/\omega$). Geometrically $J_\pm = 0$ define two surfaces in the 4-dimensional space which intersect the sphere $H = H_0$ in two circles representing the trajectories of the rotating states (see Fig. 6.7). For the corresponding probabilities we may assume the Gaussian distribution with two free parameters

$$\rho(\mathbf{r}, \mathbf{v}) = C \exp \left[-\alpha_H (H - H_0)^2 \right] \tag{6.113}$$

$$\left[\exp(-\mu J_+) + \exp(-\mu J_-) \right]. \tag{6.114}$$

We note that for the special choice $\mu = 2\alpha_H H_0$ we may bring this to the more special form

$$\rho(\mathbf{r}, \mathbf{v}) = C' \exp \left[-\frac{\mu}{2H_0}(H^2 - H_0^2) \right] \tag{6.115}$$

$$\left[\exp(+\mu \omega_0 L) + \exp(-\mu \omega_0 L) \right] \tag{6.116}$$

This way the probability will be concentrated on two tires in the phase space.

Let us summarize our findings: We used in this section the method of generalized Gibbs distributions (Gibbs, 1902; Landau & Lifshits, 1990) and in particular the Zubarev method for constructing relevant distributions (Subarev, 1976; Zubarev et al., 1996, 1997). These methods are of phenomenological character and connected with the maximum entropy approach. We repeat the basic assumptions: Due to the boundary conditions certain averages as e.g. here the angular momentum L_N or L_N^2 are prescribed. This does not mean that the quantities are fixed, only the averages or the most probable values are prescribed and fluctuations around these values which are described by the distribution are possible. The distribution function is found by maximizing the entropy of distributions which fulfill the given constraints.