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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 → statistical mechanics → 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 → statistical physics → 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 se-*

lection 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 fun-

damental role of entropy and its connection with the probability of microscopic states. Later he improved Helmholtz's chemical thermodynamics and his theory of double layers, as well as developed theories of solutions, including electrolytes, of chemical equilibrium and of the coexistence of phases. Planck was especially interested in the foundations of statistical thermodynamics. In fact he was the first who wrote down explicitely the famous formula

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

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. More-

over, 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 will prepare a separate article 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.

$$dE = d_eE + d_iE \tag{2.1}$$

$$d_iE = 0 \tag{2.2}$$

Any process is connected with a transfer d_eE 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):

$$dE = d_e E = d'Q + d'A \tag{2.3}$$

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

$$dE = d'Q + d'A + \sum_i \mu_i dN_i \tag{2.4}$$

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)

$$dE = TdS + \sum_k l_k dL_k + \sum_i \mu_i dN_i \qquad (2.11)$$

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

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

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

$$dX = d_eX + d_iX \tag{2.13}$$

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

$$dE = d_eE + d_iE, \tag{2.14}$$

$$dS = d_eS + d_iS \tag{2.15}$$

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

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

$$d_eE = d'Q + d'A + \sum_i \mu_i d_eN_i$$

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

$$dS \geq d_eS; \qquad d_iS \geq 0. \tag{2.16}$$

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

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

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

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

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 uncertainities, 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

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

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

$$\Delta S = \langle \Delta S(\infty) \rangle \qquad (2.23)$$

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

$$\Delta S = \delta S \qquad (2.24)$$

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

$$L(t) = \Delta S - \Delta S(t) \qquad (2.25)$$

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

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

Due to

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

and

$$\Delta S \geq \Delta S(t) \qquad (2.27)$$

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

$$F = E - TS \qquad (2.28)$$

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

$$dF = dE - TdS - SdT$$

$$= \sum_k l_k dL_k + \sum_i \mu_i dN_i - SdT \qquad (2.29)$$

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

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

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

$$dF = d'A - SdT - Td_iS \qquad (2.30)$$

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

$$dF = -Td_iS \leq 0; \qquad \frac{dF}{dt} = -TP \leq 0 \quad (2.31)$$

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

$$\begin{aligned} dG &= d'A - d'Q - Vdp - pdV - SdT - Td_eS - Td_iS \\ &= Vdp - SdT - Td_iS. \end{aligned} \tag{2.35}$$

For given temperature and pressure we get

$$\begin{aligned} dG &= -Td_iS \leq 0 \\ \frac{dG}{dt} &= -TP \leq 0 \end{aligned} \tag{2.36}$$

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

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

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 → 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 $S_{eq}(E, X)$ 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:

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

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

$$S = k_B \log W \quad (2.42)$$

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:

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

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

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 proba-

bility 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

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

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.

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

We will use the following notation:
(i) If $x_1,...x_n \rightarrow x_1,...,x_f$ are usual mechanical coordinates, we call the equation *Smoluchowski equation* to honour the contribution of Marian Smoluchowski (18.. - 1917).
(ii) If $x_1,...,x_n \rightarrow x_1,...,x_f,v_1,...v_f$ 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

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

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

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

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

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

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

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

such that

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

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 $x' \rightarrow x$ 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.*

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

with

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

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:

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

(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

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

(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

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

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 1D Rayleigh particle with the dynamics

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

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

(i) Find solutions without noise $D = 0$ and
(ii) study the Fokker-Planck equation in the case with noise $D > 0$.
Investigate first the case $a < 0, b = 0$ (so-called Ornstein-Uhlenbeck process) and then the case $a > 0, b > 0$ (free active Brownian particles) Find stationary solutions of the Fokker-Planck equation.