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Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems

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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 :

$$dS = \frac{d'Q}{T} \quad (3.1)$$

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

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:

$$[\mathbf{q}, \mathbf{p}] = [q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f] \quad (3.3)$$

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).

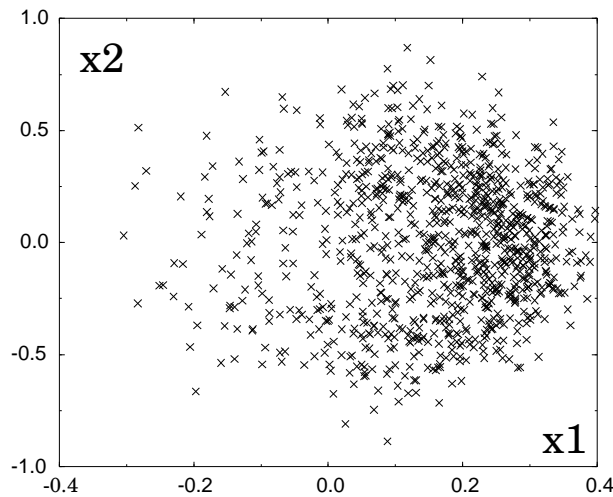


Fig. 3.1 A cloud of points in the phase space of molecules corresponding to the state of a macroscopic molecular system.

Let us define, as did already Boltzmann, the function $f(\mathbf{q}, \mathbf{p}, t)$ 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 \mathbf{q} and \mathbf{p} ; more precise we have to consider not phase points but volume elements $d\mathbf{q}d\mathbf{p}$ in the phase space. We consider $f(\mathbf{q}, \mathbf{p}, t)$ as dimensionless and take into account that the volume element in the phase space $d\mathbf{q}d\mathbf{p}$ has the dimension of an action to the power

of the space dimension. Therefore we have chosen Planck's constant h^3 as a normalization factor. Note, that 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 $f(\mathbf{q}, \mathbf{p}, t)$ is dimensionless and

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

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

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

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 $f^{eq}(\mathbf{q}, \mathbf{p})$. Instead of repeating the derivation let us simply state the central ideas. We consider two particles with the states \mathbf{q}, \mathbf{p} and $\mathbf{q}_1, \mathbf{p}_1$ before a collision. Assuming that \mathbf{q}', \mathbf{p}' and $\mathbf{q}'_1, \mathbf{p}'_1$ are the corresponding states after the collision, we expect that the products of probabilities before and after the collision are equal

$$f^{eq}(\mathbf{q}, \mathbf{p}) f^{eq}(\mathbf{q}_1, \mathbf{p}_1) = \quad (3.6)$$

$$f^{eq}(\mathbf{q}', \mathbf{p}') f^{eq}(\mathbf{q}'_1, \mathbf{p}'_1) \quad (3.7)$$

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

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

$$= \ln f^{eq}(\mathbf{q}', \mathbf{p}') + \ln f^{eq}(\mathbf{q}'_1, \mathbf{p}'_1) \quad (3.9)$$

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

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

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

$$\langle E_{kin} \rangle = \left\langle \frac{\mathbf{p}^2}{2m} \right\rangle = \frac{3}{2\beta} \quad (3.11)$$

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

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

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

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*

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

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

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

$$\cdot \ln f(\mathbf{q}, \mathbf{p}, t). \quad (3.15)$$

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, Boltzmann's 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

$$S = k_B H_B \quad (3.16)$$

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

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

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 thermo-

dynamics 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 $f(\mathbf{q}, \mathbf{p}, t)$ 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 \mathbf{q} , which is true for spatially homogeneous systems. Then we get according to Boltzmann

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

with a certain nonlinear functional I of the distribution function:

$$I[f(\mathbf{p}, t)] = \int \sigma [f(\mathbf{p}')f(\mathbf{p}'_1) - f(\mathbf{p})f(\mathbf{p}_1)] d\mathbf{p}' d\mathbf{p}'_1 d\mathbf{p}_1 \quad (3.19)$$

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

$$I[f(\mathbf{p}, t)] \simeq -\nu [f(\mathbf{p}, t) - f^{eq}(\mathbf{p}, t)] \quad (3.20)$$

The physics behind this expression is the plausible assumption that the effect of collision occurring 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

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

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

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

we may show that

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

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

$$\delta S(t) \geq 0 \quad (3.24)$$

and

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

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, \dots, q_{3N} and the $3N$ momenta p_1, \dots, p_{3N} of the macroscopic system. Gibbs' generalization of the entropy to interacting systems of point-like molecules reads:

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

where $\rho(\mathbf{q}, \mathbf{p})$ 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

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

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

$$S_{BP} = k_B \ln W. \quad (3.28)$$

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

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

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

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 pub-

lished 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

$$H_B(t_1) \leq H_B(t_2) \leq \dots \leq H_B(t_n). \quad (3.30)$$

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.

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

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 "*An-*

nalen 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 argu-

ments 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 a firm ground, Boltzmann founded the subject of ergodic theory. The aim of ergodic theory is to derive prob-

abilities 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, \dots, q_f and f momenta p_1, \dots, p_f :

$$H(q_1, \dots, q_f, p_1, \dots, p_f). \quad (3.32)$$

The equations of motions of our Hamiltonian dynamics are

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} \quad (3.33)$$

$$= -\frac{\partial H}{\partial q_i}. \quad (3.34)$$

By integration of the Hamiltonian equations at given initial state $\mathbf{q}(t), \mathbf{p}(t), i = 1, \dots, f$ 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

$$I_k(q_1, \dots, q_f, p_1, \dots, p_f) = C_k \quad (3.35)$$

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 $q_1(t), \dots, q_f(t), p_1(t), \dots, p_f(t)$ 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:

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

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 $b \rightarrow \infty$, ($ab = \text{const}$) 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

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

For an infinite uniform chain ($-\infty < n < +\infty$)

Toda (1981, 1983) found the integrals of motion

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

corresponding to the soliton energy

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

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

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

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

$$\frac{\sinh^2 \chi}{\chi} \gg 1 \quad (3.41)$$

reads according to eq.(3.35)

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

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

$$H(q_1, \dots, q_f, p_1, \dots, p_f) = E \quad (3.43)$$

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 $F(q_1, \dots, q_f, p_1, \dots, p_f)$ exists which is defined by

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

$$F(q_1(t'), \dots, q_f(t'), p_1(t'), \dots, p_f(t')) \quad (3.45)$$

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

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f)G(q_1, \dots, q_f, p_1, \dots, p_f) \rangle \quad (3.46)$$

$$= \langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle \quad (3.47)$$

$$\langle G(q_1, \dots, q_f, p_1, \dots, p_f) \rangle. \quad (3.48)$$

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

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

$$F(q_1, \dots, q_f, p_1, \dots, p_f). \quad (3.50)$$

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.

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle_t = \quad (3.51)$$

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle_s \quad (3.52)$$

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 $F(q_1, \dots, q_f, p_1, \dots, p_f)$ the time average is well defined and,
- a probability measure $\rho(q_1, \dots, q_f, p_1, \dots, p_f)$ exists (called also invariant density) such that

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle_t = \quad (3.53)$$

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle_s. \quad (3.54)$$

The ensemble average used in this condition is de-

defined as

$$\langle F(q_1, \dots, q_f, p_1, \dots, p_f) \rangle_s = \int dq_1 \dots dq_f dp_1 \dots dp_f (3.55)$$

$$F(q_1, \dots, q_f, p_1, \dots, p_f) \rho(q_1, \dots, q_f, p_1, \dots, p_f) (3.56)$$

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 mechani-

cal 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 \mathbf{T} defined by the iteration

$$\mathbf{T} : \quad x(t+1) = f(x(t)). \quad (3.57)$$

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

$$t = 0, 1, 2, 3, \dots$$

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)

$$x(t+1) = rx(t)[1 - x(t)] \quad (3.58)$$

and the tent map (Fig. 3.2)

$$\begin{aligned} x(t+1) &= rx(t) & \text{if } x &\leq 1/2 \\ x(t+1) &= r(1 - x(t)) & \text{if } x &\geq 1/2 \end{aligned} \quad (3.59)$$

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

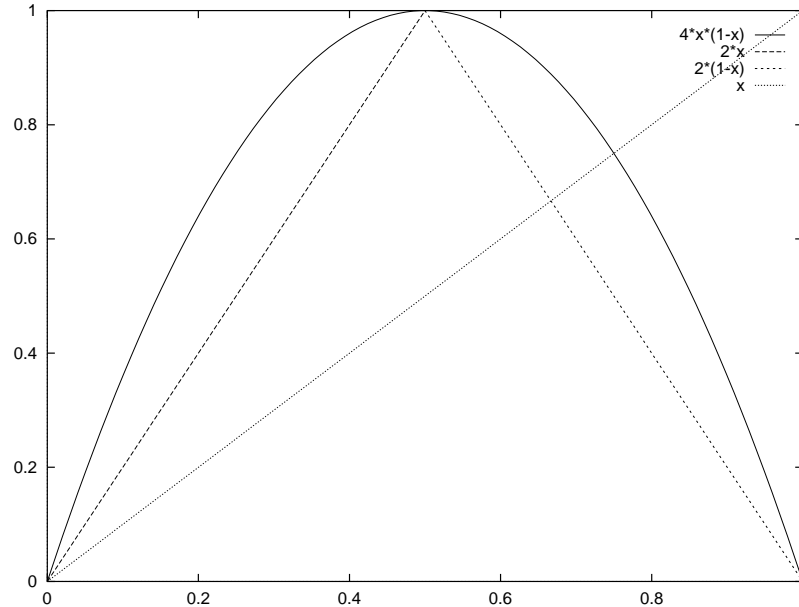


Fig. 3.2 Representation of the logistic map for $r = 4$ (a solid line) and the tent-map for $r = 2$ (a dashed line).

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

$$x_3 = rx_2(1 - x_2), \quad x_2 = rx_3(1 - x_3) \quad (3.60)$$

is born. At $r = r_2 = 1 + \sqrt{6} = 3.449\dots$ 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 occurring at the pa-

parameter values

$$r_3 = 3.544090, \quad r_4 = 3.564407 \quad (3.61)$$

$$r_5 = 3.568759, \quad r_6 = 3.569692, \dots \quad (3.62)$$

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

$$r_\infty = 3.569946\dots$$

in geometric progression

$$r_k = r_\infty - cF^{-k} \quad \text{if} \quad k \rightarrow \infty \quad (3.63)$$

with

$$c = 2.6327\dots, \quad F = 4.669202\dots$$

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

$$\lambda = \langle \phi(x(t)) \rangle_t \quad (3.64)$$

where

$$\phi(x) = \log |df(x)/dx| \quad (3.65)$$

Following an orbit of the system we may write

$$\lambda = \lim_{n \rightarrow \infty} \frac{1}{n} \sum_{k=1}^n \log |df/dx|_{x=x_k} \quad (3.66)$$

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

$$\int p(x)dx = 1. \quad (3.67)$$

For simplicity we consider only unimodal maps on the interval $0 \leq x \leq 1$; 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

$$p(x)dx = p(y)dy + p(z)dz \quad (3.68)$$

Introducing now

$$x = f(y), \quad x = f(z) \quad (3.69)$$

and

$$dx/dy = f'(y), \quad dx/dz = f'(z) \quad (3.70)$$

we get the functional relation

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

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

$$y = \frac{1}{2} - \frac{1}{2}\sqrt{1-x}, \quad z = \frac{1}{2} + \frac{1}{2}\sqrt{1-x}. \quad (3.72)$$

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

In this case the Perron-Frobenius equation assumes the form

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

One can check that the normalized solution is given by

$$p(x) = \frac{1}{\pi\sqrt{x(1-x)}} \quad \text{if} \quad 0 \leq x \leq 1. \quad (3.74)$$

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

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

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

$$p(x) = 1 \quad \text{if} \quad 0 \leq x \leq 1. \quad (3.76)$$

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

$$H = \ln\left(\frac{\pi}{4}\right). \quad (3.77)$$

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

$$H = 0 \quad (3.78)$$

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 underline 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)

$$H = \beta p - \alpha q. \quad (3.79)$$

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

$$\dot{p} = \alpha; \quad \dot{q} = \beta \quad (3.80)$$

The solutions are easily given

$$p(t) = p(0) + \alpha t; \quad q(t) = q(0) + \beta t. \quad (3.81)$$

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

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

If (α/β) is a rational number,

$$(\alpha/\beta) = m/n, \quad (3.83)$$

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

$$\langle F(q, p) \rangle_t = \langle F(q, p) \rangle_s = \int dq dp F(q, p) \quad (3.84)$$

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 $q = q_1, \dots, q_f$ and f momenta $p = p_1, \dots, p_f$. For a large class of systems the Hamiltonian is the sum of a momentum-dependent kinetic energy and a coordinate-dependent potential energy

$$H(q_1, \dots, q_f, p_1, \dots, p_f) = T(p_1, \dots, p_f) + U(q_1, \dots, q_f) \quad (3.85)$$

By integration of the Hamiltonian equations (3.34) at given initial state $q_i(t), p_i(t)$, ($i = 1, \dots, f$) 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 reversibil-

ity 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 ($i = 1, 2, \dots, f$)

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

$$p_i(t) \rightarrow p'_i(t) = -p_i(-t) \quad (3.86)$$

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

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

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

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

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 any-*

thing 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 oscil-

lations. 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 500cm^{-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 prob-

ability density

$$\rho(q_1, \dots, q_f, p_1, \dots, p_f, t) \quad (3.89)$$

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

$$\frac{d\rho}{dt} = 0. \quad (3.90)$$

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

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

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

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

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

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

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

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

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

$$\rho(q_1, \dots, q_f, p_1, \dots, p_f) = F(H(q_1, \dots, q_f, p_1, \dots, p_f)) \quad (3.95)$$

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

of this type is

$$\rho(q_1, \dots, q_f, p_1, \dots, p_f) = C \exp[-\beta H(q_1, \dots, q_f, p_1, \dots, p_f)] \quad (3.96)$$

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, \dots, 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

$$\rho(q_1, \dots, q_f, p_1, \dots, p_f) = F(I_1, \dots, I_s) \quad (3.97)$$

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 $\mathbf{x}(t) = [q_1(t), \dots, q_f(t), p_1(t), \dots, p_f(t)]$ is studied by investigating besides the original trajectories $\mathbf{x}(t; \mathbf{x}_0, t_0)$ which starts at \mathbf{x}_0, t_0 also a second one $\mathbf{x}(t; \mathbf{x}_0 + \delta\mathbf{x}_0, t_0)$, which at the initial time t_0 starts at $\mathbf{x}_0 + \delta\mathbf{x}_0$ where $\delta\mathbf{x}_0$ 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 $|\delta\mathbf{x}(t_0)| < \eta$ follows $|\delta\mathbf{x}(t)| < \epsilon$ 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 \mathbf{J} defined earlier by eq.(2.89) of the dynamical

system.

For Hamilton systems the trace of the Jacobian is zero

$$\text{Tr} \mathbf{J}(\mathbf{x}) = 0. \quad (3.98)$$

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

$$\sum_i \lambda_i = 0 \quad (3.99)$$

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

$$\lambda_1 \geq \dots \geq \lambda_j > 0 > \lambda_{j+1} \geq \dots \geq \lambda_n \quad (3.100)$$

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)

$$K_\lambda = \sum_i^+ \lambda_i, \quad (\lambda_i > 0). \quad (3.101)$$

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)

$$x(t+1) = rx(t) \quad \text{if} \quad x \leq 0.5$$

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

The time-dependent version of the Perron-Frobenius equation for the tent map is obtained by a general-

ization of eq.(3.66). Considering the balance of probabilities at time t and $t + 1$ we obtain

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

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

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

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

$$p_0(x) = 1 \quad \text{if} \quad 0 < x < 1. \quad (3.105)$$

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

$$\mathbf{P} : [C_1, \dots, C_\lambda], \quad C_i \cup C_j = 0 \quad \text{if} \quad i \neq j \quad (3.106)$$

\mathbf{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 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

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

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

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

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:

$$C_1 = [0, 0.5), \quad C_2 = [0.5, 1] \quad (3.109)$$

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 \mathbf{W} is exactly given by

$$W_{11} = 0 \quad W_{12} = 1/r^2 \quad (3.110)$$

$$W_{21} = 1 \quad W_{22} = 1/r \quad (3.111)$$

We can easily verify the Markov properties

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

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

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

$$P(2) = r/(1+r) = 0.72360... \quad (3.112)$$

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

$$C_1 = [r(1-r/2), 1/2]; \quad C_2 = [1/2, r/2] \quad (3.113)$$

$$C_3 = [0, r(1-r/2)]; \quad C_4 = [r/2, 1] \quad (3.114)$$

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

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

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 con-

sidered again as an alphabet. As shown by Nicolis et al. (1989) the corresponding probability matrix has the elements

$$W_{11} = 1/2 \quad W_{12} = 0 \quad W_{13} = 1 \quad (3.115)$$

$$W_{21} = 1/2 \quad W_{22} = 1/2 \quad W_{23} = 0 \quad (3.116)$$

$$W_{31} = 0 \quad W_{32} = 1/2 \quad W_{33} = 0. \quad (3.117)$$

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 $i = 1, \dots, s$ 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

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

This quantity is always between zero and one:

$$0 \leq \mathcal{H} \leq 1 \quad (4.2)$$

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

$$\mathcal{H} = 0 \quad \text{if} \quad p_k = 1, \quad p_i = 0 \text{ if } i \neq k \quad (4.3)$$

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

$$\mathcal{H} = 1 \quad \text{if} \quad p_i = 1/s \quad i = 1, \dots, s \quad (4.4)$$

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

$$p_{ij}^{12} = p_i^1 \cdot p_j^2 \quad (4.5)$$

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

$$\mathcal{H}^{12} = \mathcal{H}^1 + \mathcal{H}^2 \quad (4.6)$$

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

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

In the case of discrete variables $i = 1, 2, \dots, s$ 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 \mathbf{q}, \mathbf{p} : Then the Boltzmann's mean uncertainty of states in phase space is given by

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

Here $f(\mathbf{p}, \mathbf{q}, t)$ 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 di-

mension as $d\mathbf{p}d\mathbf{q}$ 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

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

with the normalization

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

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

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

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 af-

ter 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

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

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

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

or explicitly

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

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.

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

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

tropy

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

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

$$S_{BP} = k_B \ln W. \quad (4.17)$$

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

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

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 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 $E = \text{const}$) 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 micro-

scopic variables.

$$x = x(q_1, \dots, p_{3N}) \quad (4.19)$$

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)

$$\rho(p, q) = \int p(x) \cdot \rho(p, q|x) dx \quad (4.20)$$

Then a brief calculation yields

$$S_G = k_B H + S_b \quad (4.21)$$

with

$$S_b = \int p(x) S(x) dx \quad (4.22)$$

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

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

$$S_G = k_B \log 2 + S_b \quad (4.24)$$

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 :

$$E - (1/2)\delta E \leq H \leq E + (1/2)\delta E \quad (4.25)$$

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 $H(\mathbf{q}, \mathbf{p}) = E$. 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

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

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

$$S = k_B \ln \Omega^*(A) \quad (4.27)$$

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

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

Here the mysterious factor $N!$ was introduced as a consequence of the indistinguishability 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

$$S(E, t) = k \ln \Omega_{eff}^*(E, t) \quad (4.29)$$

$$\Omega_{eff}^*(E, t) = \exp[S(E, t)/k_B] \quad (4.30)$$

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

$$V_0 = V_b + V \quad (4.31)$$

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

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

Here q_1, \dots, q_{3N} and p_1, \dots, p_{3N} are the microscopic variables of the system and

$q_1^b, \dots, q_{3M}^b, p_1^b, \dots, p_{3M}^b$ 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

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

The integral is taken over the bath variables $q_1^b \dots p_{3N}^b$. 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

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

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

$$S_b(E_b, V_b) = k_B \ln \Omega(E_b, V_b) \quad (4.35)$$

By inversion of this formula we are left with

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

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

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

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 $E = H(q_1 \dots p_{3N})$ as the Hamilton function of the microscopic variables of the system and find the canonical distribution

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

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

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

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

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

The mean energy follows from the relation

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

and the dispersion is defined by

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

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.

$$N_0 = N_b + N \quad (4.43)$$

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

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

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

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

and we end with

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

By using again a normalization condition which reads now

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

we find a relation between thermodynamics and statistical quantities

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

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.

$$\Delta S = -\frac{1}{T}R_{min}. \quad (4.49)$$

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

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

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 deter-*

mined 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 $\langle A \rangle$ 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 $A = [A_1, \dots, A_m]$ 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

$$A'_k = \langle A_k \rangle = \int dqdp A_k(q, p) \rho(q, p) \quad (4.51)$$

we maximize the information entropy

$$\mathcal{H} = - \int dqdp \rho(q, p) \ln \rho(q, p) \quad (4.52)$$

under the given constraints. We define an m -component vector $\lambda = [\lambda_1, \dots, \lambda_m]$ of Lagrange multipliers. Then the probability density that agrees with the given

data \mathbf{A}' follows from

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

This leads to

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

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

$$Z(\lambda_1, \dots, \lambda_m) = \int dqdp \exp[-\sum_k \lambda_k A_k(q, p)] \quad (4.55)$$

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

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

The dispersion is given by second derivatives

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

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)

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

- Canonical ensemble:

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

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

- Grand canonical ensemble:

The case that besides the mean energy $A'_1 = E$ also the s mean particle numbers are given $A'_2 = \langle N_1 \rangle, \dots, A'_{s+1} = \langle N_s \rangle$ are given leads to the ensemble

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

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

$$H_r = H - \boldsymbol{\Omega} \cdot \mathbf{L} \quad (4.61)$$

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

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

This leads in the original system of coordinates to the distribution

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

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

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

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 situations, 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.