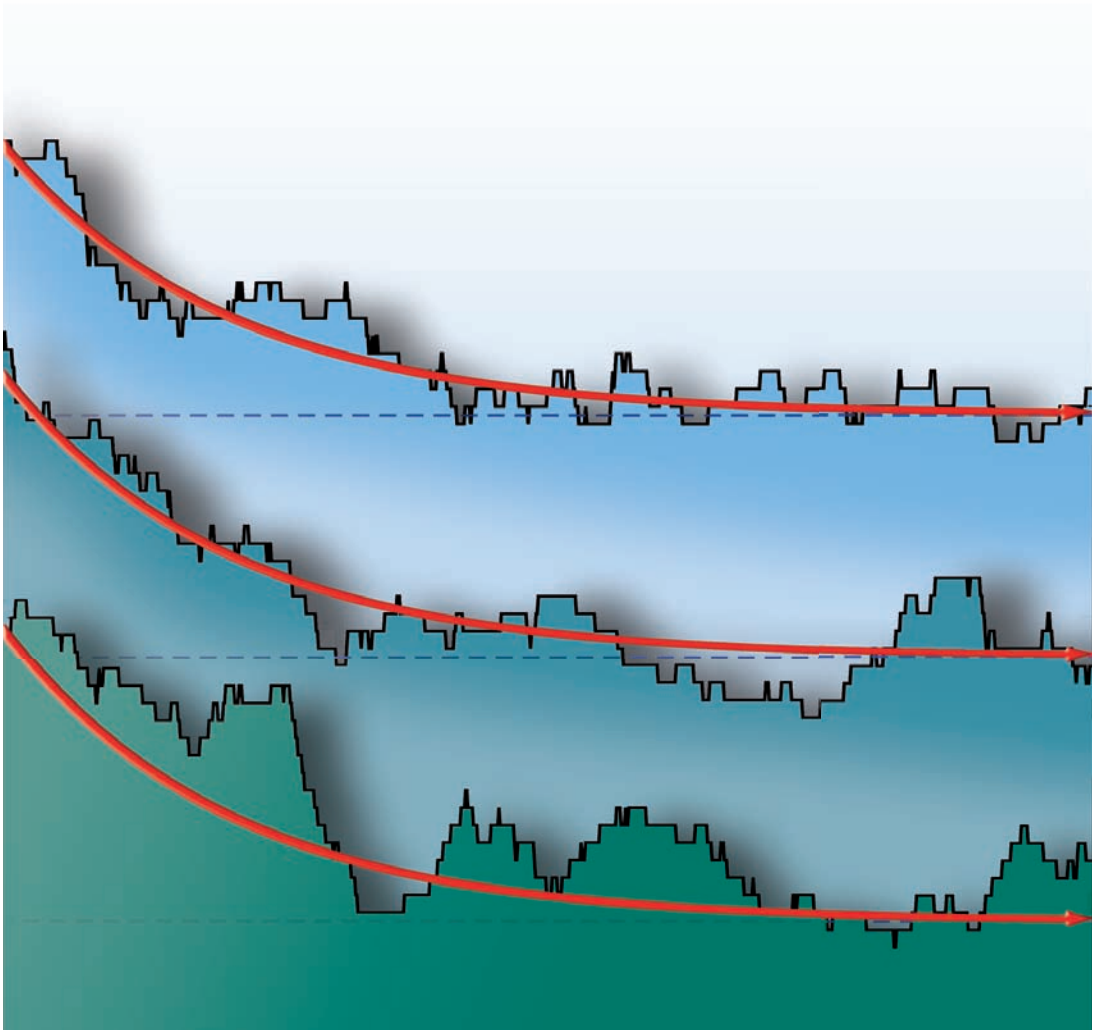


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*Dedicated to Friedrich, Franziska, Johanna, and Heide-Luise*





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## Preface

All men are like grass,  
 and all their glory is like the flowers of the field;  
 the grass withers and the flowers fall,  
 and its place remembers it no more.

– *Moses, Psalm 90: 5–6; David, Psalm 103: 15–16;*  
*Isaiah 40: 6–8; 1 Peter 1: 24–25; J. Brahms, Requiem*

Irreversibility is one of the largest mysteries of science at the present time. Birth and death, creation, evolution, and destruction are fundamental human experiences. We feel the arrow of time that determines past, present, and future. We measure time with nearly reversible, periodic processes, but there is also another aspect of time that is related to irreversible changes. It is a challenge to give a consistent approach to general nonequilibrium phenomena. Do we need new concepts and new mathematics in this context?

Nonequilibrium physics concerns different phenomena such as evolution, relaxation to equilibrium, friction, and other transport phenomena. In addition, we wish to consider the reaction of a system to external influences, the role of fluctuations, metastability and instability, pattern formation and self-organization, the role of probability and chance in contrast to a deterministic description, and the treatment of open systems. Statistical physics of nonequilibrium has created some concepts and models that are of relevance not only to physics but also to other fields such as informatics, technology, biology, medical, and social sciences. It also has an impact on fundamental philosophical questions. The treatment of nonequilibrium phenomena is an emerging field in physics and is of relevance to other fields such as quantum physics and field theories, phase transitions, bio- and nanophysics, and evolution of complex systems.

A central point is thermodynamics that introduced a new quantity, the entropy, not known in the other disciplines of theoretical physics. The second law of thermodynamics states that the entropy in an isolated system can increase but never decrease with time. Up to now, a consistent “first principle” theory of irreversible processes based on the fundamental, but reversible, equations of motion of microscopic dynamics is missing. To move toward an explanation

of irreversible phenomena, we have to inquire into some paradigms used in the present-day physics, for example, the complete separation of a system from its surroundings.

In contrast to equilibrium statistical physics, nonequilibrium statistical physics is only rarely part of current courses in theoretical physics. We are at present not able to formulate axioms or principles that allow a general approach to describe nonequilibrium physics. Only for special situations, we know different approaches that can be used to describe properties of a nonequilibrium process. In all cases, we have to add some assumptions or approximations that seem at first glance to be an inaccuracy within the strict microscopic treatment, but, on the other hand, bring a new element into the theory that seems to be indispensable to describe irreversible behavior.

A first microscopic approach to irreversible processes was given by Ludwig Boltzmann in 1873 investigating the kinetic theory of gases. The Boltzmann equation [1] that remains as a basic equation until now is based on the equations of motions for atomic collisions, but needs an additional element, the “Stoßzahlansatz” or the molecular chaos. This way, the famous H theorem explicitly shows the selection of the direction of time and the possibility to describe irreversible evolutions, starting from reversible equations of motion that describe the microscopic dynamics of the molecules.

A more systematic derivation of the Boltzmann equation was given in 1946 by Bogoliubov [2] using the principle of weakening of initial correlations. To begin with many-particle systems at low density described by the single-particle distribution function, quantum statistical methods such as the time-dependent Green’s function technique [3] have been worked out to treat also systems at higher densities. Theories for transport processes in dense systems are formulated such as the linear response theory by Kubo [4], which relates the dissipation of a nonequilibrium initial state to the evolution of fluctuations in the equilibrium system, for instance, the conductivity to current–current correlation functions.

Another approach was the projection operator technique by Nakajima and Zwanzig [5] that allowed deriving an irreversible equation, the Pauli equation, from the microscopic von Neumann equation of motion for the statistical operator. The additional assumption was that the nondiagonal elements of the density matrix are fading. This approach has been developed further to describe relaxation processes. It is presently considered in relation to decoherence and the physics of open systems.

Different nonequilibrium phenomena are described by the respective theories. The assumptions made in addition to solving the microscopic equations of motions are reasonable for the case under consideration. We have detailed monographs for different fields. As examples, the thermodynamics of irreversible processes [6], the kinetic theory [7], the linear response theory [8], different approaches in the series of Landau and Lifshits [9,10], and the theory of open systems [11,12] should be mentioned. All these approaches use some additional assumption that introduces a reduced set of relevant observables. A unified approach was given with the Zubarev method of the nonequilibrium statistical operator [13].

This book intends to give a coherent, concise, general, and systematic approach to different nonequilibrium processes. The main point of Chapter 1 is to state the problem. After discussing some basics of other cognate disciplines in theoretical physics, empirical approaches are explained. Stochastic processes like the Langevin process or random walk that are characteristic of nonequilibrium behavior are introduced in Chapter 2. Three typical domains – quantum master equations (Chapter 3), kinetic theory (Chapter 4), and linear response theory (Chapter 5) – are presented in detail. Examples are given, in particular, the radioactive decay described by a Pauli equation and the electrical conductivity in charged particle systems. Quantum statistical methods to treat many-particle systems are given in Chapter 6, concluding with an outlook in Chapter 7.

The book should make nonequilibrium statistical physics accessible to students and scientists interested or working in that field. For an extended presentation and advanced examples, refer to Refs. [14,15]. We will not divide between classical and quantum physics, but consider classical physics as a limiting case of quantum physics.<sup>1</sup> We focus on applications in solid-state physics, plasma physics, subatomic physics, and other fields where correlations are of relevance to many-particle systems. Other interesting fields, like nonequilibrium QED, phase transitions, measuring process, cosmology, turbulence, relativistic systems, and decoherence, are only briefly mentioned or even dropped.

Based on lectures given at Dresden, Rostock, Greifswald, and other places, a previous textbook was published in German [17], thanks for help in preparation to Heidi Wegener, David Blaschke, Fred Reinholz, and Frank Schweitzer. In Ref. [17], solutions are found for some problems given in the present book. A translation to Russian [18] was performed by Sergey Tischtshenko. The Green's function method was worked out as a script material by Holger Stein and improved by Mathias Winkel that served as prototype of Chapter 6. Also, the nonequilibrium statistical physics script was worked out further with the help of Jörn Schmelzer (Jr.), Robert Thiele, Thomas Millat, Carsten Fortmann, and Philipp Sperling. A lot of discussions have been performed on this subject in Rostock, Moscow, and other places. We are grateful to Dmitri Zubarev, who made me familiar with nonequilibrium thermodynamics during my postdoc stay at the Steklov Mathematical Institute of the Soviet Academy of Science, Moscow, in 1969. We also acknowledge Vladimir Morozov, Ronald Redmer, Heidi Reinholz, Werner Ebeling, Wolf-Dieter Kraeft, Dietrich Kremp, Klaus Kilimann, David Blaschke, Michael Bonitz, Thomas Bornath, Sibylle Günter, Claudia-Veronika Meister, Klaus Morawetz, Manfred Schlanges, Sebastian Schmidt, August Wierling, and others who developed quantum statistics and nonequilibrium processes during the last decades at Rostock.

Rostock, October 2012

*Gerd Röpke*

1) Note that the appearance of the classical world from quantum theory is not trivial and has to be analyzed within nonequilibrium physics [16].





## 1

## Introduction

Physics is concerned with phenomena in nature. It describes properties of systems and their time evolution. Very efficient concepts have been worked out, and detailed knowledge about nature has been accumulated. A lot of phenomena can be explained using very few basic relations. However, there also exist unsolved problems. Such a field with open questions is the physics of nonequilibrium processes, where until now no fundamental and coherent approach has been possible.

Nonequilibrium is the general situation in the real world. Change in time is one of our direct experiences; *παντα ρει*, everything flows, one does not step into the same river twice, as was pointed out by the ancient philosophers [19].

We experience dissolution, destruction, formation of new structures, higher complexity, and higher organization; possibly we believe in progress, everything is going to be alright. Evolution in biological (and social) systems is a great miracle.

Can we understand the evolution of a system and even predict the future? Why are we interested in the future? To avert danger, to optimize our situation, to realize our goals, and to see what remains. We have to make decisions and anticipate the consequences.

Physics contributes a lot by analyzing the dynamical behavior of matter. A deterministic description based on the solution of the fundamental equations of motion was promoted by its success in celestial dynamics. This formed our present approach to describe phenomena by equations of motions that have the form of differential equations. We present some fundamental equations and show that they describe reversible dynamics. Consequently, an “arrow of time” does not exist here, as detailed in Section 1.1.

The paradigm of the deterministic description is well characterized by the so-called “Laplace intelligence”: “Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective positions of the beings which compose it, if moreover this intelligence were vast enough to submit these data to analysis, it would embrace in the same formula both the movements of the largest bodies in the universe and those of the lightest atom; to it nothing would be uncertain, and the future as the past would be present to its eyes” [20].

The great success in using our fundamental equations of motions to describe all observed phenomena convinced people to believe in a deterministic approach. The exact predictability of the future, however, seems to be an illusion because of different reasons as discussed later on. In contrast to exact predictability, we introduce in Chapter 2 a probabilistic description.

We present in Section 1.2 some ideas that may contribute to the solution of the problems associated with the contradiction between irreversible evolution and reversible dynamics. We point out that the assumptions made in formulating the dynamics on the basis of the equations of motion have to be critically analyzed.

One of the basic ideas is the assumption that a system can be separated from the remaining part of the universe. Its time evolution can be described taking into account the influence of the surroundings via simple approximations.

As an example, the equations describing the motion of planets can be given neglecting the influence of astronomical objects outside the solar system. Furthermore, all the complex processes that take place on each planet are neglected. Only the center of mass motion is considered.

With respect to the motion of the planets, it is sufficient to consider only a restricted number of relevant observables characterizing the state of the system. Other observables, for example, those related to the internal state of the object, are irrelevant.

The number of relevant observables describing the state of the system is given by the degrees of freedom. One has to distinguish between the dynamical degrees of freedom, which are available by the motion of the system, and the constraints, which reduce the number of dynamical degrees of freedom.

A perfect isolation of a system from the remaining part of the universe is not possible. For example, Mach's principle relates the motion of the distant stars to the local inertial frame. It is currently not possible to disconnect gravity. As a consequence, each system also "feels" the expansion of the universe.

To make statements precise, we will give relevant results obtained in other fields of physics, known from standard courses, without extended derivations. A detailed discussion of some of the relations presented here is given later on. The corresponding references are given in the text.

## 1.1

### **Irreversibility: The Arrow of Time**

We are concerned here only with "dead" matter, particles, and their interactions. The behavior of such systems is described by "microscopic," dynamical equations of motion. Examples are the Newton equation, the Schrödinger equation, the Maxwell equations, and quantum electrodynamics.

We give some standard results and briefly show some general results from other fields of theoretical physics. Then, we discuss the irreversible "macroscopic" evolution of real systems. A detailed discussion of the equations of motion in different fields of physics is given later on. We focus only on properties with respect to time reflection, showing that there is no difference between past and future, no "arrow of time"; a reverse motion picture would also show a possible solution of the equations of motion, a possible microscopic process.

Thermodynamics [21] is a phenomenological theory, directly related to quantities that can be measured. A well-known fact is that the second law singles out an "arrow of time." In an isolated system, the entropy will increase with time for the evolution

of any nonequilibrium state. If we make a motion picture for a real phenomenon (not only friction and diffusion but also living creatures), a reverse motion picture would not show a possible real phenomenon.

As a typical example, we consider a many-particle system. The microscopic equations of motion follow from a Hamiltonian, for example, Newton's equation of motion in classical physics. For quantum systems, second quantization is very convenient to calculate properties. We also consider the statistical operator that gives a link between phenomenological properties and the microscopic dynamics. We focus here on properties with respect to time reflection and show that the equation of motion for the statistical operator, obtained from the Schrödinger equation, cannot describe irreversible processes. The appearance of the "arrow of time" in real phenomena [22] is a mystery in our present fundamental understanding of time evolution of a system using a microscopic approach.

### 1.1.1

#### Dynamical Systems

The *state* of a system at fixed time  $t$  is characterized by a number  $f$  of variables, the values of which can change with time. This number  $f$ , the *degrees of freedom*, may be finite. For example,  $f = 3$  in thermodynamics of compression processes and chemical reactions, and the variables are the volume  $\Omega$ , the particle number  $N$ , and the temperature  $T$ .<sup>1)</sup> We are concerned in the following with a system of  $N$  point masses in *classical mechanics* where  $f = 6N$  for the Cartesian components of the position and momentum vectors. It may also be infinite, for example, for fields  $\varphi(\mathbf{r}, t)$  (electrical field, state vector in quantum mechanics, etc.) where for each of an infinite number of positions  $\mathbf{r}$  in space, the corresponding value of the field must be known. Alternatively, we can characterize a field by components with respect to a (infinite) basis system of orthonormal functions.

#### Classical Mechanics

Can we predict the future of the state of the system if we know its initial state, that is, can we predict the change in the values of the state variables with time? As an example, we can consider the system of  $N$  point-like interacting particles as an idealization used in celestial mechanics<sup>2)</sup> or in molecular dynamics. The state in

1) To avoid confusion with the interaction potential, we will use  $\Omega$  instead of  $V$  for the volume.

2) Celestial mechanics gave the impression that we are able to predict the future. The problem is reduced to six degrees of freedom, position and momentum, for each body moving in a given force like the gravitational force. All further details that happen inside the bodies, for example, the processes occurring on the earth, are irrelevant for the motion of the planetary system, and the interaction with other

exoplanetary objects is small and can be neglected. This concept is very successful but cannot be taken for the ultimate truth. We have to accept that we will never have a full knowledge of all influences. In principle, we always have open systems. In addition to the relevant observables that characterize the state of the system, there is always a contact with further degrees of freedom (denoted as surroundings, reservoirs, and bath). The complete isolation of a system is an idealization.

configuration space has  $3N$  degrees of freedom. The forces are assumed to be conservative. To solve the equations of motion that define a special trajectory  $\{\mathbf{r}_1(t), \dots, \mathbf{r}_N(t)\}$ , for example, to solve the Newton equations or the Hamilton equations, we need initial conditions. The actual state in configuration space is not sufficient, we also need to have the information about the actual values of the velocities or the canonical conjugate momenta. To determine the dynamical state of the system, we have to extend the set of state variables (degrees of freedom), that is, the configuration space to the  $6N$  dimensional  $\Gamma$  space that also includes, besides the positions, the particles' momenta.

For a classical system of  $N$  particles, the dynamics is determined by the Hamilton function  $H(\mathbf{r}_j, \mathbf{p}_j)$ , which is the sum of kinetic and potential energy.

$$H(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N) = \sum_{i=1}^N \frac{1}{2m_i} \mathbf{p}_i^2 + \sum_{i=1}^N V^{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^N V(\mathbf{r}_i, \mathbf{r}_j), \quad (1.1)$$

where  $i = 1, \dots, N$  denotes the particle number. In general, the external potential  $V^{\text{ext}}(\mathbf{r})$  can be time dependent,  $V^{\text{ext}}(\mathbf{r}, t)$ , for example, charged particles in a time-dependent electrical field. The interaction potential  $V(\mathbf{r}, \mathbf{r}')$  is given by the (conservative) forces between the particles.

The Hamilton equations

$$\frac{d}{dt} \mathbf{r}_i(t) = \frac{\partial H(\mathbf{r}_j, \mathbf{p}_j)}{\partial \mathbf{p}_i}, \quad \frac{d}{dt} \mathbf{p}_i(t) = -\frac{\partial H(\mathbf{r}_j, \mathbf{p}_j)}{\partial \mathbf{r}_i} \quad (1.2)$$

are first-order differential equations in time. The trajectory  $\{\mathbf{r}_1(t), \dots, \mathbf{r}_N(t)\}$  of the  $N$  body system is determined by an initial state that is a given point in the  $\Gamma$  space. The corresponding dynamics is reversible, that is, with time inversion at  $t_{\text{inv}}$ , we construct a new trajectory  $\{\mathbf{r}_1(2t_{\text{inv}} - t), \dots, \mathbf{r}_N(2t_{\text{inv}} - t)\}$ . This “new” trajectory is also a solution of the Hamilton equations (1.2) and therefore describes a possible motion.

---

In detail, for the proof, we rename the variables of the new trajectory as indicated by a bar over the variables,  $\{\bar{\mathbf{r}}_1(\bar{t}), \dots, \bar{\mathbf{r}}_N(\bar{t})\}$ . The positions remain unchanged,  $\bar{\mathbf{r}}_i = \mathbf{r}_i$ . The time inversion  $\bar{t} - t_{\text{inv}} = -(t - t_{\text{inv}})$  with respect to the time  $t_{\text{inv}}$  also means reversal of velocities or momenta,  $\bar{\mathbf{p}}_i = -\mathbf{p}_i$ .

The Hamiltonian (1.1) remains unchanged because it is quadratic in  $\mathbf{p}_i$ . With  $d/d\bar{t} = -d/dt$  as well as  $\bar{\mathbf{p}}_i(\bar{t}) = -\mathbf{p}_i(t)$  compensating the negative signs, the new trajectory is a solution of the equations:

$$\frac{d}{d\bar{t}} \bar{\mathbf{r}}_i(\bar{t}) = \frac{\partial H(\bar{\mathbf{r}}_j, \bar{\mathbf{p}}_j)}{\partial \bar{\mathbf{p}}_i}, \quad \frac{d}{d\bar{t}} \bar{\mathbf{p}}_i(\bar{t}) = -\frac{\partial H(\bar{\mathbf{r}}_j, \bar{\mathbf{p}}_j)}{\partial \bar{\mathbf{r}}_i}. \quad (1.3)$$

The differential equations (1.3) are identical with the Hamilton equations (1.2). We conclude that the reversed trajectory  $\{\mathbf{r}_1(-t + 2t_{\text{inv}}), \dots, \mathbf{r}_N(-t + 2t_{\text{inv}})\}$  is also a solution of the Hamilton equations (1.2), that is, a possible motion of the system.

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## Quantum Mechanics

A similar situation arises in *quantum mechanics*. The state of a single particle is given by a complete set of simultaneously measurable quantities. For instance, in the case

of electron,<sup>3)</sup> we need four items of data, for example, three for the position in coordinate space ( $\mathbf{r}$ ) and one for the spin orientation ( $\sigma^z$ ). In general, the state of a particle is given by the *state vector*  $|\varphi(t)\rangle$ . It can be represented by components in different basis systems, for example, the state function  $\varphi(\mathbf{r}, \sigma^z; t) = \langle \mathbf{r}, \sigma^z | \varphi(t) \rangle$  for the electron.<sup>4)</sup> Unitary transformations relate different representations, in particular the Fourier transform for the momentum representation.

The time dependence of a quantum state is determined by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\varphi(t)\rangle = H |\varphi(t)\rangle \quad (1.4)$$

and an initial state  $|\varphi(t_0)\rangle$ . The corresponding dynamics is reversible, that is, the dynamics with time inversion also describes a possible motion, if the Hamiltonian is Hermitian. We mention that time inversion also means the adjoint complex in addition to inversion of the spin and the magnetic field.

For the proof, we use the coordinate space representation where the Schrödinger equation reads

$$i\hbar \frac{\partial}{\partial t} \varphi(\mathbf{r}, \sigma^z; t) = H \varphi_n(\mathbf{r}, \sigma^z; t), \quad H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V^{\text{ext}}(\mathbf{r}), \quad (1.5)$$

following from the matrix element:

$$\langle \mathbf{r}, \sigma^z | \left[ \frac{\mathbf{p}^2}{2m} + V^{\text{ext}}(\mathbf{r}) \right] | \mathbf{r}', \sigma'^z \rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V^{\text{ext}}(\mathbf{r}) \delta^3(\mathbf{r} - \mathbf{r}') \delta_{\sigma^z, \sigma'^z}. \quad (1.6)$$

The adjoint complex of the Schrödinger equation (1.4) is

$$-i\hbar \frac{\partial}{\partial t} \langle \varphi(t) | = \langle \varphi(t) | H^\dagger, \quad -i\hbar \frac{\partial}{\partial t} \varphi^*(\mathbf{r}, \sigma^z; t) = H^\dagger \varphi^*(\mathbf{r}, \sigma^z; t). \quad (1.7)$$

Time inversion at  $t_{\text{inv}}$  gives the time-dependent state function  $\varphi^*(\mathbf{r}, -\sigma^z; 2t_{\text{inv}} - t)$ . We rename  $\bar{\mathbf{r}} = \mathbf{r}$ ,  $\bar{\sigma}^z = -\sigma^z$ . The time inversion  $\bar{t} - t_{\text{inv}} = -(t - t_{\text{inv}})$  with respect to the time  $t_{\text{inv}}$  also means the conjugate complex of the state function,  $\bar{\varphi}(\bar{\mathbf{r}}, \bar{\sigma}^z; \bar{t}) = \varphi^*(\mathbf{r}, -\sigma^z; -t + 2t_{\text{inv}})$ , which corresponds to reversal of velocities or momenta.

We rewrite Eq. (1.7). The Hamiltonian  $H$  remains unchanged because it is Hermitian,  $H^\dagger = H$ . With  $\partial/\partial \bar{t} = -\partial/\partial t$ , compensating the negative signs, the new time-dependent state function

3) How many pieces of information are needed to determine the state of an electron? The question about the complete number of observables that determine the state of a particle is unsolved (Heisenberg). The three pieces of data  $\mathbf{r}$  that give the position in configuration space are not sufficient to determine its state, we have an additional internal degree of freedom, the spin orientation. The latter is discrete with the two values  $\uparrow, \downarrow$  with respect to a given direction. There are also other choices, momentum and spin, and hydrogen states,

that also need four pieces of data. More generally, additional internal (discrete) degrees of freedom can be added such as particle/antiparticle, as well as flavor for hadrons. This is also the subject of a future theory of elementary particles, which will not be discussed here.

4) The state function is complex valued to describe interference phenomena. In contrast to the phase of a single-particle state, the modulus is related to the probability that can be measured.

$\bar{\varphi}(\bar{r}, \bar{\sigma}^z; \bar{t})$  is a solution of the equation

$$i\hbar \frac{\partial}{\partial \bar{t}} \bar{\varphi}(\bar{r}, \bar{\sigma}^z; \bar{t}) = H \bar{\varphi}(\bar{r}, \bar{\sigma}^z; \bar{t}), \quad (1.8)$$

which coincides with the Schrödinger equation (1.5), that is, a possible time motion of the system.<sup>5)</sup>

### Quantum Many-Particle Systems

The state of a *quantum many-particle system* is characterized by a corresponding high number of degrees of freedom. In general, the particle numbers  $N_c$  of species  $c$  are not fixed (emission and absorption of photons, open systems that are defined by a given volume  $\Omega$  in space allowing particle exchange with a reservoir, chemical reactions, phase transitions, etc.), so we can use in quantum physics the Fock space, that is, the direct sum of Hilbert spaces with arbitrary particle numbers. A convenient possibility to characterize the state of a system with arbitrary particle numbers is the occupation number representation (second quantization) where the number  $n_p$  of particles in each single-particle state  $p$  is used. The basis of the Fock space is given by the occupation numbers of the different single-particle states. *Creation* ( $a_p^\dagger$ ) and *annihilation operators* ( $a_p$ ) are introduced that can be used to construct the basis of the Fock space and the matrix elements of any dynamical observable. The commutation or anticommutation relations are

$$[a_p, a_{p'}^\dagger]_- = a_p a_{p'}^\dagger - a_{p'}^\dagger a_p = \delta_{pp'}, \quad [a_p, a_{p'}]_- = [a_p^\dagger, a_{p'}^\dagger]_- = 0 \quad (1.9)$$

for bosons, and

$$\{a_p, a_{p'}^\dagger\}_+ = a_p a_{p'}^\dagger + a_{p'}^\dagger a_p = \delta_{pp'}, \quad \{a_p, a_{p'}\}_+ = \{a_p^\dagger, a_{p'}^\dagger\}_+ = 0 \quad (1.10)$$

for fermions, respectively.

The Hamiltonian of a many-particle system with interaction  $V_{c,d}(p_1, p_2; p'_1, p'_2)$  (matrix element with respect to the single-particle states  $|p\rangle$ ) is

$$H = \sum_{c,p} E_c(p) a_{c,p}^\dagger a_{c,p} + \frac{1}{2} \sum_{c,d} \sum_{p_1 p_2 p'_1 p'_2} V_{c,d}(p_1, p_2; p'_1, p'_2) a_{c,p_1}^\dagger a_{d,p_2}^\dagger a_{d,p'_2} a_{c,p'_1} \quad (1.11)$$

(the variable “species”  $c$  also contains the spin orientation. It can be included in the single-particle quantum number  $p$ ). The many-particle Hamiltonian describes the dynamical evolution of the system.

The time dependence can be transformed to the Heisenberg picture. The quantum state remains unchanged, but the dynamical operator  $A$  changes with time as

$$A(t) = e^{iH(t-t_0)/\hbar} A e^{-iH(t-t_0)/\hbar}. \quad (1.12)$$

5) In the case of a magnetic field that changes its direction with time reversal, the Hamiltonian remains invariant because of the reversal of the spin direction.

$t_0$  denotes the instant of time where the Heisenberg picture and the Schrödinger picture coincide. The corresponding equation of motion is

$$\frac{\partial}{\partial t} A(t) = \frac{i}{\hbar} [H, A(t)]. \quad (1.13)$$

Similar to the Schrödinger picture, this time dependence is reversible, the equations of motion for quantum many-particle systems are invariant with respect to time inversion and complex conjugation.

### Electrodynamics

The dynamics is also reversible in other fields of “microscopic” physics. In electrodynamics, the state is described by both the electrical and magnetic fields. In a relativistic description, we can introduce the four-vector field  $A^\mu(x)$  at  $x \equiv \{ct, \mathbf{r}\}$ , and the four-tensor of field strengths is derived from the four-potential. The equations of motion in electrodynamics, the Maxwell equations, also describe reversible motion. After time inversion and reversal of the magnetic field, the new process is also a solution of Maxwell’s equations (Problem 1.1). The quantization of the electromagnetic fields can be performed using the formalism of second quantization mentioned above.

On a very sophisticated level, we can use quantum electrodynamics to describe particles interacting with the electromagnetic field. We can consider the action  $I[\psi(x), \bar{\psi}(x), A^\mu(x)]$  or the Lagrangian of  $\mathcal{L}(x) = \mathcal{L}[\psi_s, \partial_\mu \psi_s, \bar{\psi}_s, \partial_\mu \bar{\psi}_s, A^\nu, \partial_\mu A^\nu]$ , where the state of the system is given by the real Maxwell four-vector field  $A^\mu(x)$  and the complex Dirac spinor field  $\psi_s(x)$ ,  $x = (ct, \mathbf{r})$ , where  $s$  denotes the spinor components (Problem 1.2). As we know, many phenomena in atomic physics, molecular physics, solid-state physics, plasma physics, quantum optics, liquid-state physics, ferromagnetism, superconductivity, and so on are correctly described with this Lagrangian. In particular, we obtain the Dirac equation and the Maxwell equations within the canonical formalism.

A basic property of such microscopic equations of motion is *reversibility in time*. Performing a time inversion, the resulting motion also seems to be a physically possible process. There is no principal difference between past and future. Periodic processes can be used to measure the time: earth around sun, rotation of earth, pendulum, vibration of quartz, and atomic clocks (Problem 1.3).

#### 1.1.2

### Thermodynamics

The *microscopic* description is based on different approximations and idealizations. In particular, part of the interaction that is not of relevance is dropped. Real *macroscopic* systems are described phenomenologically, introducing state variables. Some of them have a simple interpretation such as the volume  $\Omega$  and the particle number  $N_c$  of species  $c$ . Also, the energy is known from mechanics as the sum of

kinetic and potential energy. More generally, we can take the Hamiltonian to calculate the energy  $E$  of a system.

Other state variables are introduced via the laws of thermodynamics that are based on experience. These laws define the temperature  $T$ , the internal energy  $U$ , and the entropy  $S$ . As a consequence, the relation

$$dU = \delta Q + \delta A = TdS - pd\Omega + \sum_c \mu_c dN_c \quad (1.14)$$

for reversible processes is obtained. Here, only two forms of work are considered, the volume compression work (pressure  $p$ ) and the chemical work (chemical potential  $\mu_c$ ).<sup>6)</sup> Reversible processes mean quasistatic, slow changes so that at each instant of time, the system is in thermal equilibrium. The first law of thermodynamics gives the increase of internal energy  $U$ .<sup>7)</sup> We identify the internal energy  $U$  with the energy  $E$  of a system.

According to the second law, the relation  $dS = \delta Q/T$  for reversible processes defines the entropy  $S$  that is an extensive quantity. At the same time, the temperature  $T$  is defined as integrating denominator. The absolute value of the entropy is fixed by the third law of thermodynamics. For any particular system under consideration, the entropy can be determined measuring the heat capacity:

$$S(T) = \int_0^T dT' \frac{C_\Omega(T')}{T'} \quad (1.15)$$

if other variables like  $\Omega$  are fixed. For engineers, tables are available containing, besides other thermodynamic functions, also the entropy for different materials.

Allowing also for irreversible processes,

$$dS \geq \frac{\delta Q}{T} \quad (1.16)$$

6) How many variables are necessary to describe the thermodynamic state of the system? The answer is related to the work we can perform on the system. Elementary approaches discuss only the volume compression work  $-pd\Omega$ . Advanced approaches also consider chemical work  $\sum_c \mu_c dN_c$ . Further contributions to work (e.g., electrical  $E d\mathbf{P}$  (polarization), magnetic  $\mathbf{H} d\mathbf{M}$  (magnetization), deformation  $\boldsymbol{\sigma} d\boldsymbol{\mu}$ ) will extend the set of state variables of the system, so there is no basic answer to the number of thermodynamic state variables. We will discuss these questions further in the next chapter.

Another issue refers to extensive (system:  $\Omega, N_c, P, M$ ) versus intensive (bath:

$p, \mu_c, E, H$ ) variables. Infinite homogeneous systems are idealizations. External forces, surface effects, phase separation, droplet formation, and so on, demand the treatment of inhomogeneities.

7) The absolute value depends on the gauge, that is, the choice of the zero of  $U$ . In particular, the potential energy has to be fixed, or the binding energy of molecules can be taken into account. Physical processes are connected only with the increase of internal energy so that an additive constant becomes irrelevant. However, the absolute value of energy determines the time dependence of the phase of a quantum state.



according to the second law. In particular,

$$\frac{d}{dt}S(t) \geq 0 \quad (1.17)$$

holds for the time evolution of the entropy of closed systems. For isolated systems, no exchange of heat with a bath is possible so that  $\delta Q = 0$ . Irreversible processes define a direction (arrow) of time because time inversion means that entropy would decrease in closed systems. More generally, for  $\bar{S}(\bar{t}) = S(t)$  with  $\bar{t} = 2t_{\text{inv}} - t$ ,

$$d\bar{S} \leq \frac{\delta Q}{T} \quad (1.18)$$

for any process. This is forbidden according to the second law of thermodynamics.

The basis for introducing the entropy is the existence of reversible and irreversible processes [21]. Three examples are discussed that establish irreversible processes: friction that transforms mechanical work into heat (e.g., pendulum with friction), diffusion of a substance to free space (e.g., dissolution of a concentration profile in a liquid), and heat transfer from warm to cold systems. It is impossible to construct a *perpetuum mobile* of the second kind. There is an arrow of time, and it becomes evident that the arrow of time points from the past into the future considering processes such as friction, heat conduction, and diffusion processes. Thus, the evolution of a real, macroscopic system is in general *irreversible*. We can distinguish between a movie of a possible process and the time inverse movie that is not possible (Problems 1.4 and 1.5).

### 1.1.3

#### Ensembles and Probability Distribution

In *thermodynamic equilibrium*, a connection between macroscopic and microscopic approaches can be given in the frame of statistical physics. For this, the entropy has to be introduced into the microscopic dynamical approach, which is done via probability. Once the entropy is introduced, other quantities like temperature or chemical potentials can be deduced.

Ensembles are considered instead of a particular real system. The ensembles are determined by all realizations that are compatible with the boundary conditions, given by the values of the relevant thermodynamic variables. More precisely, a probability distribution for the microstates of the dynamical system is introduced. This probability distribution is formed in such a way that the values of the relevant variables of the thermodynamic macrostate are correctly described (consistency conditions). As in quantum mechanics, we investigate only averaged properties of the ensemble, not the individual properties of the particular real system under consideration.

For quantum systems, the microstates of the dynamical system at time  $t$  are given by the state vector  $|\phi_n(t)\rangle$ . We suppose a complete set of commuting observables that uniquely define the microscopic state of the system, for example, the position and

z-component of spin of all electrons in a system of electrons. The distribution function or statistical operator<sup>8)</sup>

$$\rho(t) = \sum_n |\phi_n(t)\rangle w_n \langle\phi_n(t)| \quad (1.19)$$

contains the probability  $w_n$  that the macroscopic system under consideration is found in the microscopic state  $|\phi_n(t)\rangle$ . The probabilities are real numbers, so  $\rho(t)$  is Hermitian. If we have a complete set of alternative states  $|\phi_n(t)\rangle$ , the probability is normalized according to

$$1 = \sum_n w_n = \text{Tr}\{\rho(t)\}. \quad (1.20)$$

For any dynamical observable  $A$ , the average is given by<sup>9)</sup>

$$\langle A \rangle^t = \sum_n w_n \langle\phi_n(t)|A|\phi_n(t)\rangle = \text{Tr}\{\rho(t)A\}. \quad (1.21)$$

How does the statistical operator depend on time? We start with the Schrödinger equation that describes the time dependence of the states  $|\phi_n(t)\rangle$  and its conjugate complex ( $H^\dagger=H$ ):

$$i\hbar \frac{\partial}{\partial t} |\phi_n(t)\rangle = H|\phi_n(t)\rangle, \quad -i\hbar \frac{\partial}{\partial t} \langle\phi_n(t)| = \langle\phi_n(t)|H. \quad (1.22)$$

With

$$\frac{\partial}{\partial t} \rho(t) = \sum_n \left[ \frac{\partial}{\partial t} |\phi_n(t)\rangle \right] w_n \langle\phi_n(t)| + \sum_n |\phi_n(t)\rangle w_n \left[ \frac{\partial}{\partial t} \langle\phi_n(t)| \right], \quad (1.23)$$

we obtain the von Neumann equation as the equation of motion for the statistical operator:

$$\frac{\partial}{\partial t} \rho(t) + \frac{i}{\hbar} [H, \rho(t)] = 0. \quad (1.24)$$

The von Neumann equation describes reversible dynamics. The equation of motion is based on the Schrödinger equation. Time inversion and conjugate complex means that both terms change the sign, since  $i \rightarrow -i$  and both the Hamiltonian and the statistical operator are Hermitian (Problem 1.6).

8) In general, the density matrix  $\rho_{mm'}(t) = \langle\psi_{m'}|\rho(t)|\psi_m\rangle$  with respect to an arbitrary complete orthonormal basis  $|\psi_m\rangle$  may also contain nondiagonal elements. Whereas the diagonal elements  $\rho_{mm}(t)$  have the meaning of probabilities, the nondiagonal elements ( $m \neq m'$ ) express quantum interferences. It is a basic problem how to introduce a basis in which we can assume that the density matrix is

diagonal. We will discuss the related problem of entanglement and decoherence in Chapter 3.

9) The introduction of the trace allows us to formulate averages independent of the choice of the basis in the Hilbert (fixed particle number  $N_c$ ) or Fock space (arbitrary particle numbers). Averages that are introduced in the eigenrepresentation of  $\rho(t)$  are given in a form independent of the representation.

## 1.1.4

**Entropy in Equilibrium Systems**

In thermodynamic equilibrium, the state of the system is not changing with time,  $(\partial/\partial t)\rho_{\text{eq}}(t) = 0$ . There is no dependence on  $t$ . The solution of the von Neumann equation becomes trivial,

$$\frac{i}{\hbar} [H, \rho_{\text{eq}}] = 0 \quad (1.25)$$

in thermodynamic equilibrium, and the time-independent statistical operator  $\rho_{\text{eq}}$  commutes with the Hamiltonian. We conclude that  $\rho_{\text{eq}}$  depends only on constants of motion  $C$  that commute with  $H$ . However, the von Neumann equation is not sufficient to determine how  $\rho_{\text{eq}}$  depends on constants of motion  $C$ .<sup>10)</sup>

We consider a system containing particles of species  $c$  with numbers  $N_c$ . The dynamics is described by the Hamiltonian  $H$ . The thermodynamic state variables are given by the contact with the “environment” (bath or reservoir). Due to these contacts, the constants of motion  $C_n$  can fluctuate, but equilibrium means that the average values  $\langle C_n \rangle^t$  are not changing with time. *Equilibrium statistical mechanics* is based on the following principle to determine the statistical operator  $\rho$ :

Consider the functional (*information entropy*)<sup>11)</sup>

$$S_{\text{inf}}[\rho] = -\text{Tr} \{ \rho \ln \rho \} \quad (1.26)$$

for arbitrary  $\rho$  that are consistent with the fixed conditions:

$$\text{Tr} \{ \rho \} = 1 \quad (1.27)$$

(normalization) and

$$\text{Tr} \{ \rho C_n \} = \langle C_n \rangle \quad (1.28)$$

(self-consistency conditions). With these conditions, we vary  $\rho$  and determine the maximum of the information entropy for the optimal distribution  $\rho_{\text{eq}}$ .

10) This is a genuine problem in the dynamical description. We can calculate the trajectory as a solution of a differential equation, but we must have in addition information about the initial values to select a special solution. For example, Newton’s law allows to predict the positions of the planets, but does not answer the question why we have these planets with their particular parameters. For this, we have to investigate the evolution of the planetary system.

11) This definition of the equilibrium entropy, introduced by Boltzmann, Gibbs, Shannon, and Jaynes, satisfies important properties such as extensivity and validity of the thermodynamic relations. It measures the information contained in a probability distribution and can be applied to more general situations. Other entropy concepts have been introduced by Renyi [23] and Tsallis [24] that are not extensive.

The corresponding result

$$S_{\text{eq}}[\rho_{\text{eq}}] = -k_B \text{Tr} \{ \rho_{\text{eq}} \ln \rho_{\text{eq}} \}, \quad (1.29)$$

is the *equilibrium entropy* of the system for given constraints  $\langle C_n \rangle$ ,  $k_B = 1.38065 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$  is the Boltzmann constant. The solution of this variational principle leads to the Gibbs ensembles for thermodynamic equilibrium<sup>12)</sup> (see Sections 1.1.6 and 1.2.2).

As an example, we consider an open system that is in thermal contact and particle exchange with reservoirs. The sought-after equilibrium statistical operator has to obey the given constraints normalization,  $\text{Tr} \{ \rho \} = 1$ , thermal contact with the bath so that

$$\text{Tr} \{ \rho H \} = U = u\Omega, \quad (1.29a)$$

and particle exchange with a reservoir so that

$$\text{Tr} \{ \rho N_c \} = n_c \Omega. \quad (1.29b)$$

Looking for the maximum of the information entropy functional,  $S(\beta, \Omega, \mu) = \max \{ k_B S_{\text{inf}}[\rho] \}$ , with these constraints, one obtains the grand canonical distribution (see also Section 1.2.2 for derivation):

$$\rho_{\text{gr can}} = \frac{e^{-\beta(H - \sum_c \mu_c N_c)}}{\text{Tr} e^{-\beta(H - \sum_c \mu_c N_c)}} \quad (1.30)$$

or

$$w_{\text{gr can}, \nu} = \frac{e^{-\beta(E_\nu - \sum_c \mu_c N_c)}}{\sum_{\nu'} e^{-\beta(E_{\nu'} - \sum_c \mu_c N_{\nu'})}}, \quad (1.31)$$

where we introduced explicitly the eigenvalue  $N_c$  of the particle number operator,  $\nu = \{N_c, n\}$  contains the particle numbers  $N$  of all species and the internal quantum number  $n$  of the excitation,  $E_{N_c, n}$  are the energy eigenvalues of the eigenstates  $|\phi_{N_c, n}\rangle$  of the system Hamiltonian  $H$  confined to the volume  $\Omega$  (we do not use  $V$  to avoid confusion with the potential). The normalization is explicitly accounted for by the denominator (partition function). The second condition (1.29a) means that the energy of a system, which is in heat contact with a thermostat, fluctuates around an averaged value  $\langle H \rangle = u\Omega$  with the given density of internal energy  $u$ . This condition is taken into account by the

12) Various ensembles are defined by the corresponding contact of the system with its surroundings. Through this, different (extensive) thermodynamic variables  $C_n$  are introduced that characterize properties of the system. The corresponding (intensive) Lagrange parameters express the properties of the “bath.” The meaning of different ensembles and “natural” variables becomes obvious. Thermodynamic potentials are generated in a systematic way. The equations of state relate the averaged values of  $C_n$  with the given

constraints prescribed by the “bath.”

We have fluctuations of the properties of the system due to the interaction with the “bath.” We can relate this to the second derivatives of the partition function that have the meaning of material properties (e.g. specific heat, compressibility, and susceptibilities). The maximum condition of the entropy introduces stability relations for small fluctuations. In the case of thermodynamic instability, phase transitions will occur.

Lagrange multiplier  $\beta$  that must be related to the temperature, a more detailed discussion leads to  $\beta = 1/(k_B T)$ . Similarly, the contact with the particle reservoir fixes the particle density  $n_c$ , introduced by the Lagrange multiplier  $\mu_c$  that represents the chemical potentials.

Within the variational approach, the Lagrange parameters have to be eliminated. This leads to the equations of state  $\langle H \rangle = U(T, \Omega, \mu_c)$ ,  $\langle N_c \rangle = \Omega n_c(T, \mu_c)$  (Problem 1.7). The dependence of extensive quantities on the volume  $\Omega$  is trivial. The method to construct statistical ensembles from the maximum of entropy under given conditions, which take into account the different contacts with the surrounding bath, is well accepted in equilibrium statistical mechanics and is applied to different phenomena, including phase transitions (see Refs [9,13]).

In conclusion, in thermodynamic equilibrium, a connection between the microscopic dynamical approach and the thermodynamical approach can be given. For this, the entropy has to be introduced into the microscopic dynamical approach. This is done with the help of probability.<sup>13)</sup>

Can we use this definition of equilibrium entropy for evolution in *nonequilibrium* processes? Time evolution of  $\rho$ , Eq. (1.24), is given by a unitary transformation that leaves the trace invariant. Thus, the entropy defined above is constant.

More directly, from the *Liouville–von Neumann equation* as the equation of motion for the statistical operator (Eq. (1.24)),

$$\frac{\partial}{\partial t} \rho(t) + \frac{i}{\hbar} [H, \rho(t)] = 0. \quad (1.32)$$

Considering the time variation on the right-hand side of Eq. (1.29), we find

$$\frac{d}{dt} [-k_B \text{Tr} \{ \rho(t) \ln \rho(t) \}] = 0. \quad (1.33)$$

(For the proof we can use the series expansion  $\ln [1 + (x - 1)] = (x - 1) - (x - 1)^2/2 \pm \dots$  and for each power of  $\rho(t)$  apply the relation (1.32) and invariance of the trace with respect to cyclic changes of operators.)

The equations of motion, including the Schrödinger equation and the Liouville–von Neumann equation, describe reversible processes and are not appropriate for describing irreversible processes. Therefore, the entropy concept (1.29) worked out in equilibrium statistical physics cannot be used as a fundamental approach to nonequilibrium statistical physics.

Up to now, there is no basic approach for how to extend the concept of entropy to nonequilibrium processes. There are different situations where equations of evolution can be given, which contain, in addition to the dynamical description, phenomenological concepts (e.g., the Boltzmann equation and the “Stoßzahlansatz”). In this book, we attempt the formulation of a coherent description applicable to different nonequilibrium processes. We indicate clearly where additional arguments are introduced to obtain irreversible equations of evolution that do not conflict with equilibrium descriptions.

13) There are different individual systems that form the ensemble. This is a virtual ensemble of systems, without any interaction between these virtual systems. The entropy is an observable for a real system and can be measured. Can it depend on the other virtual members that form the ensemble?

## 1.1.5

**Fundamental Time Arrows, Units**

The problem of treating irreversible processes is connected with the *arrow of time*. Past, present, and future are different. Is there a common, general phenomenon that defines the arrow of time? Various processes are known where the time direction is singled out [22].

- 1) The *condition of radiation* in electrodynamics (retarded solution) and the boundary conditions for the scattering process in quantum physics describe an irreversible process. Sommerfeld's radiation condition, the condition of outward radiation, selects the retarded solution of the wave equation (Problem 1.11).
- 2) The second law of *thermodynamics* defines the arrow of time. In thermodynamics of irreversible processes, transport coefficients are introduced that are related to fluctuations in equilibrium. In hydrodynamics, conductive transport, viscosity, thermal conductivity, and so on produce dissipation to equilibrium. The theory of turbulence describes nonequilibrium evolution. Relaxation to equilibrium occurs for chemical reactions, spin systems, and so on. Master equations, kinetic equations, and linear response theory describe irreversible processes and are the subject of this book.
- 3) In *quantum mechanics*, two different time evolutions are known for a quantum state, the Schrödinger equation, which is a reversible equation of motion, and the process of measuring, which describes the irreversible evolution of a quantum state under the influence of an (classical) apparatus. During this process, quantum coherence is lost.
- 4) In *elementary particle physics*, the *CPT* theorem is known that states that processes are invariant with respect to the simultaneous transformation *C* (antiparticles), *P* (inversion of space), and *T* (inversion of time). Processes are known such as the decay of  $K^0$  mesons, which violate *CP* invariance and thus also *T* invariance, that is, single out a time direction.
- 5) In *astrophysics*, the thermodynamics of black holes is not invariant with respect to time inversion; matter falls into the black hole and disappears.
- 6) In *cosmology*, general relativity describes an expanding universe, characterized by the Hubble constant.<sup>14)</sup> This gives the arrow of time.

An interesting question is whether there exists a “master arrow of time” that also defines the other observed arrows of time.

The following issues are also of importance in connection with irreversibility:

- *Chaotic motion*. The equation of motion for dynamical systems can show *dynamical instabilities*, so the trajectory becomes unpredictable over long time intervals. This happens in particular for complex systems. The Lyapunov exponent indicates
- 14) The expansion of the Universe gives a relation between the distance  $r$  and the radial velocity (“recession velocity”),  $v_r = t_{\text{Hubble}}^{-1} r$ . The Hubble time is  $t_{\text{Hubble}} = 4.35 \times 10^{17}$  s or 13.8 billion years.