Preface

The development of thermodynamics, or more precisely "phenomenological thermodynamics", began in the early 19th century with the invention and extensive operation of steam engines. Contrary to classical point mechanics, devised by Isaac Newton and his followers starting in the 17th century, thermodynamics is based on the assumption that matter, like a fluid, a gas, or a solid, has the form of a deformable continuum that fills the whole space. Such a continuum can normally be described by very few material parameters (heat capacity, density, elasticity, etc.), and as a consequence its present state is defined by very few state variables, such as temperature or pressure. The description of processes where heat and its transformation to mechanical work play a crucial role was not feasible in the frame of Newton's mechanics. Later it turned out that the concepts of thermodynamics are very general and can be applied to other scientific branches, such as chemical reactions, biological, or nowadays even social questions.

Students of sciences or engineering normally study a basic course of one or two semesters on thermodynamics, restricted to "processes" in thermal equilibrium. In fact, the quotation marks denote a contradiction: time plays essentially no role in equilibrium physics, because one of the definitions of equilibrium is time independence of all variables. But "process" means variation and transformation from a given state to another one, and processes in thermal equilibrium can at most "run" infinitely slowly. At least for the normally taught equilibrium thermodynamics, the notion "thermostatics" would be much more appropriate.

On the other hand, all natural processes, biological, astrophysical, or geophysical, to name but a few, take place far from equilibrium. Life itself is a constant fight against equilibrium that is eventually, but unavoidably, reached after death. Thus studying nonequilibrium thermodynamics seems not only be important for the physicist.

Processes far from equilibrium normally run in a unique direction; they are called "irreversible." A precious wine glass falls down from the table and breaks into pieces while its potential energy is finally transformed in heat energy, heating up the pieces and the surrounding air. The inverse process: the air and the pieces cool down and put their heat energy first into the creation of the very same antique glass and later into kinetic energy needed to lift the glass from the floor back to the table, can be excluded. Both processes are possible from the point of energy conservation, and both are far from equilibrium. But the broken pieces on the floor are much closer to equilibrium than the glass on the table. In the first case, equilibrium is approached; in the reverse one it would be abandoned.

A measure for the distance from equilibrium is entropy. The closer a system is to equilibrium, the higher is its entropy. A process running versus equilibrium will thus act as a source for entropy. It produces entropy as long as it is out of equilibrium. We shall call such a process a "natural process." Of course the backwards process to a natural process can be performed, but a lot of machinery and manpower, for our example, amongst

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others, an experienced glassblower, would be necessary. At the end, this endeavor would produce much more entropy as that lost from reconstruction of the glass on the table.

But how is entropy defined? First introduced by Rudolf Clausius in 1865, entropy is a state function as energy and at least its changes can be measured and computed. Every thermodynamic system has a certain value of entropy, which is unique for a given state. In a closed (isolated) system, all natural processes increase the total entropy. The entropy reaches a maximum if the system is in equilibrium. This is the second law of thermodynamics. Entropy and its production is a central concept in non-equilibrium thermodynamics. The distance from equilibrium is proportional to the amount of entropy production per time. But this distance can also be interpreted as the source for generalized forces that create fluxes, which drive the system towards equilibrium. The fluxes are associated with densities, such as energy and momentum of the continuum by conservation laws. The conservation laws have the form of partial differential equations and are well known, for instance, as heat equation, Navier–Stokes equations, and continuum equation, or in multi-component systems, as reaction-diffusion equations.

Thermodynamics can be considered as the science of macroscopic objects, where the microscopic or atomic level plays no role. However, if the microscopic world would be ruled by classical mechanics, Newton's equations of motions should apply for the microscopic particles. Such a hypothesis indicates a bridge between Newton's microscopic world and thermodynamic theories. This bridge was identified in the second half of the 19th century, mainly by James Clerk Maxwell and Ludwig Boltzmann. Heat was defined as internal energy of microscopic particles and temperature as the mean deviation of particle velocities from a mean velocity. Boltzmann connected the disorder of a microscopic gas to the value of the so-called H-functional that plays the role of the macroscopic (negative) entropy. With his nowadays called "H-theorem," he could prove that the H-functional in a closed system always decreases, putting the second law on purely mechanical grounds. In this way, Boltzmann could solve the old riddle how on the microscopic level a bunch of gas particles moving reversibly can lead to irreversible macroscopic behavior with a pronounced direction of the time arrow. Here we only mention a serious objection against Boltzmann's reasoning raised by Josef Loschmidt in 1876: What if one considers a gas of many particles on its way to equilibrium and suddenly *reverse all* particle velocities? If the microscopic physics is reversible, the gas then must move "backwards" towards states with lower and lower entropy and depart from equilibrium. This apparent contradiction to the H-theorem (and to the second law) is nowadays known as "Loschmidt's paradox," "irreversibility paradox" or "Umkehreinwand." For details and its "solution" we refer to the discussion in Chapter 8.

Energy and entropy are the two pillars of all natural sciences, and hence far from being only important in thermodynamics. Each is ruled by one of the two fundamental thermodynamic laws. If we assume that our world is closed and isolated, the two laws have very general consequences:

(I) The total energy of the universe is constant.
(II) The total entropy of the universe can never decrease.

In the long time limit, the universe will come to thermal equilibrium and all energy will be transformed into heat in form of radiation. The formation and the existence of patterns such as those of clouds, waves, stones, plants or animals can only be temporary, accounting for a locally limited decrease of entropy. Nevertheless, the total entropy thereby increases.

From the brief sketch outlined above several important notions and keywords can be gathered. The present textbook tries to explain these fields and put them into a common frame. A sort of assignment of the keywords to the book chapters is the following:

- state of a system and state variables, Chapter 1;
- internal energy and heat, Chapters 1–4;
- thermal equilibrium and non-equilibrium, Chapters 1, 2;
- irreversible processes, Chapters 2–6;
- entropy and irreversibility, Chapters 1, 2;
- conservation laws, Chapters 2, 3;
- self-organized pattern formation, Chapters 5, 6;
- bridge between microscopic (Newton's) and macroscopic world, Chapters 7–9.

The reader should be acquainted with the subject of equilibrium thermodynamics, as it is taught for instance in a basic course of theoretical physics in a bachelor degree programme. Many examples are studied and applications from fluid dynamics and chemical non-equilibrium reactions are discussed in detail. In the second part, the phenomenologically derived transport equations from the first part are put on statistical grounds following Boltzmann's kinetic theory of gases.

The rest of the book is organized as follows: Chapter 1 repeats the prerequisites, fundamental laws, and notions from equilibrium thermodynamics. Chapter 2 is the central chapter of the first part of the book and introduces conservation laws and a formula for entropy production, valid outside of equilibrium. Multi-component systems, i. e., mixtures of gases or fluids and chemical reactions, are thereby discussed in detail. in Chapter 3, the famous Onsager relations are applied in relation to conservation equations, and a set of partial differential equations or transport equations is presented. Chapters 4 to 6 show many applications coming from heat conduction, diffusion processes, chemical reactions, and hydrodynamics. Thereby, the emergence of instabilities followed by self-organized macroscopic pattern formation occurs quite naturally.

The second part is based on the kinetic gas theory devised by Ludwig Boltzmann and gives a statistical foundation for the equations and relations illustrated in the first part of the book. Starting with some general considerations of a classical many particle system in Chapter 7, the Boltzmann equation is stated and the H-theorem is proven in Chapter 8. In Chapter 9, the transport equations phenomenologically outlined in Chapter 3 are derived applying the relaxation time approximation. Finally, numerical solutions of the Boltzmann equation are presented for two simple problems and compared with solutions of the transport equations of the first part.