THE STATISTICAL MECHANICS OF IRREVERSIBLE PHENOMENA

This book provides a comprehensive and self-contained overview of recent progress in nonequilibrium statistical mechanics, in particular, the discovery of fluctuation relations and other time-reversal symmetry relations. The significance of these advances is that nonequilibrium statistical physics is no longer restricted to the linear regimes close to equilibrium but extends to fully nonlinear regimes. These important new results have inspired the development of a unifying framework for describing both the microscopic dynamics of collections of particles, and the macroscopic hydrodynamics and thermodynamics of matter itself. The book discusses the significance of this theoretical framework in relation to a broad range of nonequilibrium processes, from the nanoscale to the macroscale, and is essential reading for researchers and graduate students in statistical physics, theoretical chemistry, and biological physics.

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In memory of Grégoire Nicolis

Contents

Preface

Time asymmetry is observed in many phenomena, which are referred to as irreversible. At the macroscale, the arrow of time is expressed by the second law of thermodynamics in terms of the so-called entropy. Yet, at the microscale, the laws of electrodynamics and mechanics are symmetric under time reversal. Irreversibility and microreversibility are often opposed, and we may wonder how such contrasted aspects may be compatible with each other.

Recent advances in statistical mechanics are shedding a new light on this issue. Since pioneering work by Maxwell and Boltzmann, statistical mechanics has been building a bridge between the motion of atoms and molecules composing matter and its macroscopic properties. During recent decades, discoveries in the nanosciences have revealed the existence of diverse molecular structures and processes on all the scales intermediate between the size of atoms and the macroscopic world, this latter being usually characterized by the Avogadro number equal to $N_A = 6.02214076 \times 10^{23}$ particles per mole.[1] With covalent bonds, atoms can form large molecules such as fullerenes and carbon nanotubes, as well as arbitrarily long macromolecules. Nanoclusters with a few hundred atoms may undergo liquid–solid transitions (Haberland et al., 2005). Chemical nanoclocks can manifest themselves in heterogeneous catalytic reactions, as observed with field ion microscopy (McEwen et al., 2009). Single-electron transport and irreversibility are measured in submicrometric semiconducting quantum dots (Küng et al., 2012). In biological cells, linear and rotary molecular motors made of proteins can perform mechanical power developing about 10^{-18} W (Alberts et al., 1998). More generally, the metabolism and the self-reproduction of biological cells are driven by nanometric enzymes dissipating energy.

At the nanoscale, thermal and molecular fluctuations are prevailing due to the atomic structure of matter, so that statistical mechanics plays a fundamental role in the description of such small systems. Statistical mechanics supplements the laws of mechanics by making assumptions on the initial and boundary conditions for externally prepared or controlled systems, and by methods to predict the properties of the systems from these assumptions. Indeed, the laws of mechanics formulated by Newton, Hamilton, Schrödinger, and others are based on ordinary or partial differential equations, leaving unspecified the initial and

[1] By its historical definition as an SI unit, this number refers to artefacts such as the kilogram and, thus, probably more to human muscular strength than to any property of the inanimate world of atoms.

boundary conditions. In this regard, the symmetry under time reversal can be considered either for the equations of motion, which define microreversibility, or for the initial conditions, which concern the statistical level of description. This key point is used, in particular, to establish the so-called fluctuation relations, which constitute a major advance in statistical mechanics, allowing us to understand today the properties of irreversible phenomena on the basis of the reversible microscopic dynamics of atoms and electrons.

The aim of this book is to provide a comprehensive overview of these advances in statistical mechanics. For this purpose, the successive chapters explain how statistical mechanics can make predictions by linking together different theories, including thermodynamics, hydrodynamics, and the theory of stochastic processes.

Chapter 1 presents thermodynamics, where the equilibrium and nonequilibrium properties can be identified using the second law of thermodynamics.

Chapter 2 is devoted to statistical mechanics, where the concepts of statistical ensembles and probability distributions are introduced on the basis of classical mechanics. In this framework, the distinction between equilibrium and nonequilibrium statistical ensembles can be made by considering their symmetry under time reversal. The concept of entropy is associated with the probability distributions describing the system. Moreover, linear response theory and the fluctuation-dissipation theorem are formulated in the classical setting and the projection-operator methods are summarized.

The deduction of hydrodynamics from the underlying microscopic dynamics is carried out in Chapter 3 by considering local equilibrium distributions. The method is shown to extend to the phases of matter with broken continuous symmetries such as crystals and liquid crystals.

In Chapter 4, the theory of stochastic processes is elaborated for physicochemical systems described as Markovian processes. In this context, the rate of entropy production is deduced and the Hill–Schnakenberg network theory is explained. The case of Brownian motion is used to illustrate how the probabilistic description can be inferred from statistical mechanics.

The fluctuation relations are presented in Chapter 5, first for the nonequilibrium work and then for the energy and particle fluxes across open systems in contact with several reservoirs. Their deduction is performed on the basis of microreversibility in the framework of classical statistical mechanics, leading to exact fluctuation relations and the connection to entropy production. Furthermore, the fluctuation relations are shown to have fundamental consequences about the linear and nonlinear response properties. The Onsager–Casimir reciprocal relations are found for the linear response properties. Their generalizations up to arbitrarily high orders are obtained for the nonlinear response properties. Moreover, the multivariate fluctuation relation for the currents is also established within the theory of stochastic processes using the Hill–Schnakenberg network theory.

In Chapter 6, path probabilities and temporal disorder are defined and their properties under time reversal are inferred, showing that the rate of entropy production can be related to time asymmetry in temporal disorder. The analogy with other symmetry-breaking phenomena is discussed.

Chapters 7–13 apply the previous results to different types of nonequilibrium processes.

Chapter 7 deals with driven Brownian particles and analogous electric circuits, as well as to related stochastic processes.

The case of effusion processes is presented in Chapter 8, for which the fluctuation relation and the connection between the entropy production and the time asymmetry in temporal disorder can be directly proved from mechanics.

The processes ruled by Boltzmann's kinetic equation in dilute and rarefied gases are studied in Chapter 9, where the fluctuation relation for the energy and particle fluxes is obtained from the fluctuating Boltzmann equation.

Chapter 10 presents several processes where fluctuation relations can be obtained from fluctuating chemohydrodynamics: transport by diffusion, diffusion-influenced surface reactions, ion transport, diodes, transistors, and Brownian motion described by non-Markovian generalized Langevin processes deduced from fluctuating hydrodynamics.

The stochastic approach to reactive systems is developed in Chapter 11, where fluctuation relations are obtained for chemical reactions.

Chapter 12 considers several cases of active processes: transmembrane ion transport, molecular motors, and chemically propelled Janus particles. In these active processes, energy transduction is ruled by a fluctuation relation for the fluxes that are coupled together.

In Chapter 13, transport is studied using Hamiltonian dynamical models. The periodic Lorentz gases and the multibaker map are used to investigate deterministic diffusion and to mathematically construct the diffusive modes on the basis of the microscopic dynamics. Fourier's law for heat conduction is shown to hold in many-particle billiard models. Furthermore, the importance of the nonlinear response properties is illustrated with models for mechanothermal coupling.

The last two chapters are concerned with quantum systems. Quantum statistical mechanics is summarized in Chapter 14, showing how quantum master equations and stochastic Schrödinger equations can be deduced with methods similar to those used in Brownian motion theory. Finally, transport in open quantum systems is presented in Chapter 15, where the fluctuation relation for the energy and particle fluxes is established within the framework of quantum mechanics. Systems with interacting and noninteracting particles are considered. The scattering approach is developed for the full counting statistics of noninteracting particles and for their temporal disorder. The Onsager–Casimir reciprocal relations and their generalizations beyond the linear regime are shown to hold in quantum as well as classical systems. The transport properties are described in particular for fermions, bosons, and electrons in mesoscopic devices such as quantum dots, quantum point contacts, and single-electron transistors.

Several appendices provide complements on thermodynamics, dynamical systems theory, statistical mechanics, hydrodynamics, stochastic processes, and fluctuation relations.

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