A Kinetic View of Statistical Physics

Aimed at graduate students, this book explores some of the core phenomena in nonequilibrium statistical physics. It focuses on the development and application of theoretical methods to help students develop their problem-solving skills.

The book begins with microscopic transport processes: diffusion, collision-driven phenomena, and exclusion. It then presents the kinetics of aggregation, fragmentation, and adsorption, where basic phenomenology and solution techniques are emphasized. The following chapters cover kinetic spin systems, by developing both a discrete and a continuum formulation, the role of disorder in non-equilibrium processes, and hysteresis from the nonequilibrium perspective. The concluding chapters address population dynamics, chemical reactions, and a kinetic perspective on complex networks. The book contains more than 200 exercises to test students' understanding of the subject. A link to a website hosted by the authors, containing an up-to-date list of errata and instructor solutions to the exercises, can be found at www.cambridge.org/9780521851039.

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Preface

Statistical physics is an unusual branch of science. It is not defined by a specific subject per se, but rather by ideas and tools that work for an incredibly wide range of problems. Statistical physics is concerned with interacting systems that consist of a huge number of building blocks – particles, spins, agents, etc. The local interactions between these elements lead to emergent behaviors that can often be simple and clean, while the corresponding few-particle systems can exhibit bewildering properties that defy classification. From a statistical perspective, the large size of a system often plays an advantageous, not deleterious, role in leading to simple collective properties.

While the tools of equilibrium statistical physics are well-developed, the statistical description of systems that are out of equilibrium is less mature. In spite of more than a century of effort to develop a formalism for non-equilibrium phenomena, there still do not exist analogs of the canonical Boltzmann factor or the partition function of equilibrium statistical physics. Moreover, non-equilibrium statistical physics has traditionally dealt with small deviations from equilibrium. Our focus is on systems far from equilibrium, where conceptually simple and explicit results can be derived for their dynamical evolution.

Non-equilibrium statistical physics is perhaps best appreciated by presenting wideranging and appealing examples, and by developing an array of techniques to solve these systems. We have attempted to make our treatment self-contained, so that an interested reader can follow the text with a minimum of unresolved methodological mysteries or hidden calculational pitfalls. Our main emphasis is on exact analytical tools, but we also develop heuristic and scaling methods where appropriate. Our target audience is graduate students beyond their first year who have taken a graduate course in equilibrium statistical physics and have had a reasonable exposure to mathematical techniques. We also hope that this book will be accessible to students and researchers in computer science, probability theory and applied mathematics, quantitative biological sciences, and engineering, because a wide variety of phenomena in these fields also involve the time evolution of systems with many degrees of freedom.

We begin with a few "aperitifs" – an abbreviated account of some basic problems along with some hints at methods of solution. The next three chapters comprise the major theme of transport processes. Chapter 2 introduces random walks and diffusion phenomena, mechanisms that underlie much of non-equilibrium statistical physics. Next, we discuss collision-driven phenomena in Chapter 3. We depart from the tradition of entirely focusing on the Boltzmann equation and its application to hydrodynamics. Instead, we emphasize pedagogically illuminating and tractable examples, such as the Lorentz gas and Maxwell models. In Chapter 4, we give a brief overview of exclusion processes and the profound consequences that exclusion has on transport and the spatial distribution of particles.

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Preface

The next three chapters discuss the kinetics of aggregation, fragmentation, and adsorption. The classic aggregation process – in which two clusters irreversibly merge to form a larger cluster – serves as a rich playground to illustrate exact solution methods and the emergence of scaling in cluster size distributions. Many of these technical lessons will be applied throughout this book. Our presentation of the complementary process of fragmentation follows a similar logical development. We then treat the irreversible adsorption of extended objects onto a surface. Here a kinetic approach provides a remarkably easy way to solve the seemingly difficult geometric problem of determining the final coverage of the surface.

Chapters 8 and 9 are devoted to non-equilibrium spin systems. We first focus on kinetic Ising models because of their simplicity and their broad applicability to dynamic phenomena associated with phase transitions. The following chapter on coarsening develops a meso-scopic picture, in which the elemental degrees of freedom are droplets and interfaces, rather than the atomistic spins of the kinetic Ising model. These two viewpoints are complementary and each provides valuable insights. Chapter 10 gives a glimpse into the role of disorder for three specific examples of non-equilibrium processes. The next chapter exploits the insights gained from studying spin systems and disorder to treat the phenomenon of hysteresis.

Chapters 12 and 13 are devoted to population dynamics and the kinetics of chemical reactions. The first of these two chapters also treats the role of discreteness. This feature can lead to time evolution that is much different from that predicted by the deterministic rate equations. The following chapter focuses on the essential role of spatial fluctuations and dimension-dependent effects on reaction kinetics. We close with a presentation of the master equation approach to understand the basic properties of complex networks. As in the case of adsorption, the kinetic viewpoint leads to a powerful and intuitive way to determine many geometrical properties of networks.

We conclude each chapter with a short "Notes" section that provides a guide to additional reading. We primarily direct the reader to books and review articles. By this emphasis, we do not mean to slight original literature, but most relevant information can be found within these more comprehensive references. However, we do cite original sources when such an exposition is particularly useful pedagogically or when a particular subject has not yet been reviewed.

Our choice of topics has been guided by the desire to provide key ideas and core techniques that will help turn students of non-equilibrium statistical physics into practitioners. Owing to space limitations as well as our own lack of knowledge and personal biases, many important topics have been omitted. Nevertheless we hope that a student who successfully studies from this book will then be ready to competently assimilate many other topics in non-equilibrium statistical physics by self-study.

Although our coverage of topics is incomplete, the contained material is still too ambitious for a one-semester course. For such a course, we recommend most of Chapter 2 (random walks/diffusion), the first three sections of Chapter 3 (collisions), the first four sections of Chapter 5 (aggregation), sections 7.1 and 7.4 in Chapter 7, most of Chapters 8 and 9 (spin systems and coarsening), the first two sections of Chapter 12 (population dynamics), the first three sections of Chapter 13 (diffusive reactions), and Chapter 14 (complex networks).

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Preface

Students are encouraged to solve the problems; this is perhaps the most effective way to learn the material.

We owe a great debt of gratitude to numerous collaborators, colleagues, and students who have helped shape our thinking and who have also provided advice in the preparation of this book. Each of us has benefited from insights learned from long-term collaborators, and some of their insights have percolated their way into this book. We do not mention them by name because they are too numerous and we are sure to miss some. Nevertheless, we are truly grateful to them, and we are lucky to count many of these colleagues and co-authors among our friends.

We are also grateful to many Boston University graduate students who enrolled in a course in non-equilibrium statistical physics that was based on material in this book and was taught by two of us (PLK and SR). Their questions and feedback on preliminary versions of chapters of this book have been extremely helpful. We especially thank Boston University students Luca D'Alessio, Kip Barros, and David Schaich for their careful reading of portions of the book and their helpful comments. We have also benefited from the feedback of students in mini-courses based on this book at the NSF-sponsored Boulder Summer School and at the Perimeter Scholars Institute sponsored by the Perimeter Institute for Theoretical Physics. We thank several of our colleagues for reading early drafts of this book and for providing many useful suggestions and corrections. This includes Dani ben-Avraham, Harvey Gould, Jon Machta, and Mauro Mobilia. We are especially grateful to Kirone Mallick who read the entire book and provided numerous suggestions for improvements.

Two of the authors (PLK and SR) wish to thank the National Science Foundation for providing research funding over an extended period that helped in our writing of this book. EB is grateful to Los Alamos National Laboratory for continued support of his work. We would be grateful to receive errata and will maintain an up-to-date list of errata on our websites. Feel free to contact any of the authors: paulk@bu.edu (PLK), redner@bu.edu (SR), or ebn@lanl.gov (EBN).

Conventions

One of the pleasures of working in statistical physics is that there is almost no need to specify the units; it is sufficient to remember that (in classical non-relativistic physics) there are only three independent units of mass, length, and time. This is a welcome return to normality, especially after going through electrodynamics and magnetism, a beautiful subject that has been muddled by the SI system of units. In statistical physics there is one such intruder from the SI system, Boltzmann's constant k, and many physicists and even mathematicians proudly display this worthless conversion factor. Boltzmann's constant is a lesser evil than artifices such as the permittivity or the permeability of the vacuum, but keeping k is akin to carrying the conversion factor between miles and kilometers. Throughout this book the Boltzmann constant is always one, k = 1; that is, temperature is measured in energy units.

Non-equilibrium statistical physics has a substantial overlap with applied mathematics and we follow valuable lessons from the latter, e.g. we try to work with equations in dimensionless form. Whenever we use dimensionful equations, we try to employ dimensional analysis which often leads to spectacular advances with minimal effort. Dimensional analysis originated in hydrodynamics, a subject that is also on the disciplinary boundary between non-equilibrium statistical physics and applied mathematics.

For the sake of notational simplicity, we commit some abuses in notation. For example, we use the same letter for a function and its Fourier transform, say f(x) and f(k), respectively. By context, there is rarely a risk of confusion and this convention allows us to avoid cluttered notation. Similarly, we write the Laplace transform of a function f(x) as f(s); for the Mellin transform of f(x) we also write f(s). Since the Laplace and Mellin transforms never appear together, the redundancy of notation should not cause any confusion.

Some technical conventions: throughout this book an overdot always means differentiation with respect to time. The meaning of the relational symbols \equiv , \cong , \sim , \sim , \propto , \approx , etc., is usually fuzzy in the minds of every researcher, and we can attest that it has caused us headaches throughout the preparation of this book. To keep mathematical relations simple and minimal, we tried to avoid the symbols \cong , \propto , and \approx because they are not far from the symbols \equiv , \simeq , and \sim . Specifically:

- \cong has a meaning intermediate between \equiv and \simeq , so we use one of the extremes;
- \propto has a meaning that resembles \sim , so we use \sim ;
- \approx often gives the approximate numerical value of a constant; since nowadays we can easily extract as many digits as we like, there is minimal need for this symbol.

Thus we primarily use the symbols that are defined as follows:

 \equiv indicates "defined as";

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	\simeq indicates "asymptotically equal to"; for example, $\sin 2x \simeq 2x$ when $x \to 0$; ~ means "proportional" (say $\sin 2x \sim x$); more generally, ~ means "of the order of"; of
	course, we prefer the standard equal sign whenever we are writing an exact solution; \Rightarrow means equality to as many digits as we like, but we only quote the first few; for

example, $\sqrt{2} \doteq 1.41421356$.