STATISTICAL MECHANICS OF NONEQUILIBRIUM LIQUIDS

SECOND EDITION

In recent years the interaction between dynamical systems theory and nonequilibrium statistical mechanics has been enormous. The discovery of fluctuation theorems as a fundamental structure common to almost all nonequilibrium systems, and the connections with the free-energy calculation methods of Jarzynski and Crooks, have excited both theorists and experimentalists. This book charts the development and theoretical analysis of molecular dynamics as applied to equilibrium and nonequilibrium systems.

Substantially updated and revised, this book is designed both for experts in the field and beginning graduate students of physics. It connects molecular-dynamics simulation with mathematical theory to understand nonequilibrium steady states. It also provides a link between the atomic, nano, and macro worlds, showing how these length scales relate. The book ends with an introduction to the use of nonequilibrium statistical mechanics to justify a thermodynamic treatment of nonequilibrium steady states, and gives a direction to further avenues of exploration.

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Preface to the second edition

Since 1990, when the first edition appeared, there has been a significant advance in the development of nonequilibrium systems. The centerpiece of the first edition was the nonequilibrium molecular-dynamics methods and their theoretical analysis, the connections between linear and nonlinear response theory, and the design of the simulation methods. This is now a mature field with only one significant addition, which is the new method for elongational flows.

Chapter 10 in the first edition was called "Towards a thermodynamics of steady states." This contained an introduction to deterministic chaotic systems. The second edition has the same title for Chapter 10, but the contents are now completely different. The application of the ideas of modern dynamical-systems theory to nonequilibrium systems has grown enormously with all of Chapter 8 devoted to this. However, this still constitutes the barest of introductions with whole books (Gaspard, 1998; Dorfman, 1999; Ott, 2002; and Sprott, 2003) devoted to this theme. The theoretical advances in this area are some of the biggest. The development of methods to study the time evolution using periodic orbits, and the use of periodic orbits to develop SRB measures for nonequilibrium systems are exciting steps forward.

Based on the dynamical properties, Lyapunov exponents in particular, there have been great strides made in the development of the study of fluctuations in nonequilibrium systems. The fluctuation theorems, and methods for calculating free-energy differences using nonequilibrium paths, have dominated conferences for the last 6–7 years. The additional fact that these can be tested in real (rather than computer) experiments and used to measure free-energy differences in the unfolding of biological molecules will have a large impact.

Thanks are due to many people. Customarily we thank our wives, and remark that they are still the same! To those that have led the development of statistical mechanics and inspired and mentored those that followed we owe a great debt: Eddie Cohen, Bob Dorfman, Siegfried Hess, Christian Gruber, and many others.

A number of people were especially generous with their time for which we are very grateful, in particular, Peter Daivis, Carl Dettmann, Tooru Taniguchi, and Debra Bernhardt (Searles). Special thanks also to Billy Todd, Tom Hunt, Lamberto Rondoni, Chris Angstmann, David Kruss, Anthony Whelan, Dean Robinson, David Monaghan and Tony Chung. I am very pleased to acknowledge the contribution of Ian Watson, who as an undergraduate student read and learnt from this book, in the process discovering (and helping to correct) many of its faults. As ever, Eddie Cohen was a frustrating inspiration to us all!

I feel the pull of the white ship at the Grey Havens in the long firth of Lune.

Preface to the first edition

During the 1980s there have been many new developments regarding the nonequilibrium statistical mechanics of dense classical systems. These developments have had a major impact on the computer simulation methods used to model nonequilibrium fluids. Some of these new algorithms are discussed in the recent book by Allen and Tildesley (1987), *Computer Simulation of Liquids*. However, that book was never intended to provide a detailed statistical mechanical backdrop to the new computer algorithms. As the authors commented in their preface, their main purpose was to provide a working knowledge of computer simulation techniques. The present volume is, in part, an attempt to provide a pedagogical discussion of the statistical mechanical environment of these algorithms.

There is a symbiotic relationship between nonequilibrium statistical mechanics on the one hand and the theory and practice of computer simulation on the other. Sometimes, the initiative for progress has been with the pragmatic requirements of computer simulation and at other times, the initiative has been with the fundamental theory of nonequilibrium processes. Although progress has been rapid, the number of participants who have been involved in the exposition and development, rather than with application, has been relatively small.

The formal theory is often illustrated with examples involving shear flow in liquids. Since a central theme of this volume is the nonlinear response of systems, this book could be described as a text on theoretical rheology. However our choice of rheology as a test-bed for theory is merely a reflection of personal interest. The statistical mechanical theory that is outlined in this book is capable of far wider application.

All but two pages of this book are concerned with atomic rather than molecular fluids. This restriction is one of economy. The main purpose of this text is best served by choosing simple applications.

Many people deserve thanks for their help in developing and writing this book. Firstly we must thank our wives, Val and Jan, for putting up with our absences, our irritability, and our exhaustion. We would also like to thank Dr. David MacGowan for reading sections of the manuscript. Thanks must also go to Mrs. Marie Lawrence for help with indexing. Finally special thanks must go to Professors Cohen, Hanley, and Hoover for incessant argument and interest.