An Introduction to Chaos in Nonequilibrium Statistical Mechanics

14

CAMBRIDGE LECTURE NOTES IN PHYSICS

J. R. DORFMAN

An Introduction to Chaos in Nonequilibrium Statistical Mechanics

J. R. DORFMAN
Institute for Physical Science and Technology
and
Department of Physics
University of Maryland
College Park, Maryland

CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, UK www.cup.cam.ac.uk
40 West 20th Street, New York, NY 10011–4211, USA www.cup.org
10 Stamford Road, Oakleigh, Melbourne 3166, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain

First published 1999

Printed in the United Kingdom at the University Press, Cambridge

Typeset by the Author [CRC]

A catalogue record for this book is available from the British Library

Library of Congress Cataloguing in Publication data
Dorfman, J. Robert (Jay Robert), 1937–
An introduction to chaos in nonequilibrium statistical mechanics /
J. R. Dorfman
p. cm. – (Cambridge lecture notes in physics 14)
Includes bibliographical references and index.
ISBN 0 521 65589 7 (pbk.)
1. Statistical mechanics. 2. Chaotic behavior in systems.
I. Title. II. Series.
QC174.8.D67 1999
530.13′01′1857–dc21 98–50545 CIP

ISBN 0 521 65589 7 paperback

An Introduction to Chaos in Nonequilibrium Statistical Mechanics

This book is an introduction to the applications in nonequilibrium statistical mechanics of chaotic dynamics, and also to the use of techniques in statistical mechanics important for an understanding of the chaotic behaviour of fluid systems.

The fundamental concepts of dynamical systems theory are reviewed and simple examples are given. Advanced topics including SRB and Gibbs measures, unstable periodic orbit expansions, and applications to billiard systems, are then explained. The text emphasises the connections between transport coefficients, needed to describe macroscopic properties of fluid flows, and quantities, such as Lyapunov exponents and Kolmogorov–Sinai entropies, which describe the microscopic, chaotic behaviour of the fluid. Later chapters consider the roles of the expanding and contracting manifolds of hyperbolic dynamical systems and the large number of particles in macroscopic systems. Exercises, detailed references and suggestions for further reading are included.

This book will be of interest to graduate students and researchers, with a background in statistical mechanics, working in condensed matter physics, nonlinear science, theoretical physics, mathematics and theoretical chemistry.

JAY ROBERT DORFMAN attended the John Hopkins University, receiving a BA degree in chemistry in 1957, and a PhD degree in physics in 1961. Professor Dorfman then spent three years as a post-doctoral fellow at the Rockefeller University before moving to the University of Maryland as an Assistant Professor in the Institute for Fluid Dynamics and Applied Mathematics (now the Institute for Physical Science and Technology) and the Department of Physics and Astronomy. He was promoted to the rank of Professor in 1972. During the years 1983–1992 Professor Dorfman served as Director of the Institute for Physical Science and Technology, the Dean of the College of Computer Mathematical and Physical Sciences, the Vice President for Academic Affairs and Provost of the University of Maryland at College Park. Currently he is engaged in research on the relation between dynamical systems theory and non-equilibrium statistical mechanics.

CAMBRIDGE LECTURE NOTES IN PHYSICS 14

General Editors: P. Goddard, J. Yeomans

1. Clarke: The Analysis of Space-Time Singularities
3. Sciama: Modern Cosmology and the Dark Matter Problem
4. Veltman: Diagrammatica – The Path to Feynman Rules
5. Cardy: Scaling and Renormalization in Statistical Physics
6. Heusler: Black Hole Uniqueness Theorems
7. Coles and Ellis: Is the Universe Open or Closed?
8. Razumov and Saveliev: Lie Algebras, Geometry, and Toda-type Systems
9. Forshaw and Ross: Quantum Chromodynamics and the Pomeron
10. Jensen: Self-organised Criticality
11. Vanderzande: Lattice Models of Polymers
12. Esposito: Dirac Operators and Spectral Geometry

This book is dedicated to my wife Celia, to our children and grandchildren, and to the memory of our granddaughter Abby, whose laughter brought us joy, and whose courage gave us strength.

Preface

v'Ha-aretz hayta tohu va'vohu...v'ruach Elohim merahefet al pnai ha-mayim.

Now the earth was unformed and void ... and the spirit of God hovered over the face of the waters.

Genesis, 1.2

This book began its life as a set of lecture notes based on a series of lectures given to fourth year students at the Institute for Theoretical Physics at the University of Utrecht during the spring semester of 1994. The course of lectures was entitled *From Molecular Chaos to Dynamical Chaos.* At the suggestion of Prof. Matthieu Ernst, two students in the class, Lucas Neevens van Baal and Iris Lafaille, took notes, edited them, and prepared a LaTeX manuscript that formed the basis for the lecture notes. The notes have undergone several revisions and many more corrective exercises to remove many errors that I inadvertently added to the original LaTeX file provided by Mr. van Baal and Ms. Lafaille. It is due to their hard work and desire to make the notes as clear as possible that the notes have made their reappearance as a book.

I would like to thank the students who attended the course in Utrecht and those who have used the lecture notes at the University of Maryland since then. One of the original students in Utrecht, Ramses van Zon, and some students at Maryland, Rainer Klages, Thomas Gilbert, Debabrata Panja, and Luis Nasser, have

taken the subjects discussed here as Ph.D. theses topics, which, of course, is a pleasant outcome of any series of lectures to advanced students. I want to thank them as well as the many other students and colleagues who have attended my lectures for helping me understand and clarify many of the points presented here.

I would like to thank my colleagues at the Institute for Theoretical Physics, University of Utrecht, for their warm hospitality, their generous help, and their creatively critical attitude, which was always refreshing. It is a pleasure to thank two colleagues in particular, Matthieu Ernst and Henk van Beijeren, for all of their help, support, and advice, and for many fruitful scientific collaborations, which have continued for over thirty years and have now evolved to collaborations on topics related to those covered in these lectures. Much of the clarity that this book may have is due in large part to many discussions, especially with Profs. Ernst and van Beijeren, and also with Drs Donald Jacobs and Harmen Bussemaker. It is a pleasure to thank Prof. Nico van Kampen for interesting discussions on quantum chaos and on linear response theory. I would also like to express my gratitude to Ms. Leonie Silkens for her help on many matters during my stay in Utrecht.

My colleagues at the University of Maryland, Mischa Brin and Garrett Stuck of the Department of Mathematics, and especially those in the chaos group, Edward Ott, Brian Hunt, Celso Grebogi, and James Yorke provided me with a first-rate education in dynamical systems theory and chaos, and have been encouraging of my efforts to relate their field to mine, statistical mechanics. My colleagues in the Institute for Physical Science and Technology, particularly Profs. Jan Sengers, Ted Kirkpatrick, Dave Thirumalai, and John Weeks, have been helpful indeed in welcoming me back to research after a period in administration. Thanks are also due to the Institute for Physical Science and Technology, the Department of Physics, the Office of the Dean of the College of Computer, Mathematical and Physical Sciences, and the Office of the Vice-President for Academic Affairs at the University of Maryland at College Park for various forms of financial and logistical support.

I especially want to thank Masao Yoshimura, Arnulf Latz, Rainer Klages, Charles Ferguson, Mihir Arjunwadkar and Kenneth Snyder for their considerable help in getting the book in its final form,

for teaching me a great deal about LaTeX and computers in general, and for their valuable scientific support. Prof. John Weeks kindly provided Figure 2.1. I am indebted to Charles Ferguson for the figures of the cat map in Chapter 8. Thanks are also due to Prof. Michel Droz, Mr. Jerome Magnin, and the Department of Physics of the Univsersity of Geneva for their kind hospitality during May-June, 1998, when some parts of this book were written.

Much of what is new in this book is due to very happy scientific collaborations that I have had with Henk van Beijeren, Pierre Gaspard, Matthieu Ernst, E. G. D. Cohen, Shuichi Tasaki, Harald Posch, Rainer Klages, Arnulf Latz, Cecile Appert, Donald Jacobs, Christoph Dellago, Charles Ferguson, Debabrata Panja, and Thomas Gilbert. Prof. Predrag Cvitanović was kind enough to use a version of this text in a course at Northwestern University, and provided me with a number of corrections and helpful remarks. I thank him and his students at Northwestern for their suggestions and advice. Masao Yoshimura, Arnulf Latz, Rainer Klages, Ernest Barreto, Jane Gaily, Kenneth Snyder, Thomas Gilbert, Mihir Arjunwadkar, Karol Zyczkowski, Carl Dettmann, Juergen Vollmer, Támas Tél, Raul Rechtman, Pierre Gaspard, Luis Nasser, and David Urbach also read large parts of the text and made many valuable and significant suggestions for improvement. I am very indebted to Howard Weiss for a critical reading of the manuscript, which led to many improvements in the book, as well as for several important references to papers in the mathematical literature. Critical remarks by Jean Bricmont and anonymous referees led to a number of clarifications at various important points in the text and I thank Prof. Bricmont, especially, for his interesting and very stimulating thoughts on a number of matters.

There are two individuals to whom I owe a special debt of gratitude. Prof. Pierre Gaspard of the Université Libre de Bruxelles has aided me enormously in my understanding of the connections between nonequilibrium statistical mechanics and dynamical systems theory both through his writings and through our collaboration on a number of interesting topics. I wish to thank Prof. E. G. D. Cohen of the Rockefeller University who through many years of close and fruitful collaboration, has helped shape my understanding of irreversible processes.

The English translation of the Hebrew text from Genesis is used with permission of the Jewish Publication Society. The Hebrew phrase, 'tohu va'vohu', has entered a number of languages (English, French,...) as 'tohubohu', meaning 'chaos', 'disorder', or 'confusion'.

Finally, I would like to acknowledge support from the National Science Foundation under Grants No. PHY-93-21312 and PHY-96-00428.

A web site has been established for this book, at the time of publication. This web site can be accessed through the author's home page at http://www.ipst.umd.edu/dorfman.

J. R. Dorfman
College Park, Maryland
December, 1998

Contents

1
Nonequilibrium statistical mechanics

1.1 Introduction

Statistical mechanics is a very fruitful and successful combination of (i) the basic laws of microscopic dynamics for a system of particles with (ii) the laws of large numbers. This branch of theoretical physics attempts to describe the macroscopic properties of a large system of particles, such as one would find in a fluid or solid, in terms of the average properties of a large ensemble of mechanically identical systems which satisfy the same macroscopic constraints as the particular system of interest. The macroscopic phenomena that concern us in this book are those which fall under the general heading of irreversible thermodynamics, in general, or of fluid dynamics in particular. We shall be concerned with the second law of thermodynamics, more specifically, with the increase of entropy in irreversible processes. The fundamental problem is to reconcile the apparent irreversible behavior of macroscopic systems with the reversible, microscopic laws of mechanics which underly this macroscopic behavior. This problem has actively engaged physicists and mathematicians for well over a century.

1.2 The law of large numbers and the laws of mechanics

Many features of the solution to this problem were clear already to the founders of the subject, Maxwell, Boltzmann, and Gibbs, among others. The notion that equilibrium thermodynamics and fluid dynamics have a molecular basis is one of the central scientific advances of the 19th century. Of particular interest to us here is the work of Maxwell and Boltzmann, who tried to understand the laws of entropy increase in spontaneous natural processes on the basis of the classical dynamics of many-particle systems. Boltzmann's derivation, in 1872, of what is now known as the Boltzmann transport equation was a major step in the process of making the connection between molecular motions and irreversible thermodynamics. Boltzmann considered a dilute gas of particles interacting with short-range, central, pairwise forces, and obtained, using what appeared to be completely mechanical arguments, an equation for the distribution function, $F(\mathbf{r}, \mathbf{v}, t)$, of particles in a small region, $\delta\mathbf{r}$ about a point at position $\mathbf{r}$, with velocity in the range $\delta\mathbf{v}$ about velocity $\mathbf{v}$ at time t. This equation, which we will derive in the next chapter, has the interesting property that one can define a function of time, $H(t)$, in terms of the distribution function, which decreases monotonically in time, and reaches a constant value when the velocity distribution function is the Maxwell–Boltzmann equilibrium distribution system is spatially uniform. Furthermore, when evaluated for a system with this equilibrium distribution, the H-function is exactly $-S/k_{\text{B}}$, where S is the thermodynamic entropy for an ideal gas, and k_{B} is Boltzmann's constant.

Consequently, Boltzmann had *almost* achieved the resolution of thermodynamics with mechanics, at least for dilute gases, by identifying this H-function with the negative of the thermodynamic entropy.

Objections were raised to Boltzmann's derivation of the laws of irreversible thermodynamics, based upon the time-reversal invariance of Newton's equations of motion and upon the Poincaré recurrence theorem. The former objection (called *Loschmidt's paradox*) says that if there is a motion of the gas that leads to a steady decrease of H with time, then there is certainly another allowed state of motion of the system, found by time reversal, in which H must increase. The second objection is a bit more subtle. Poincaré had proved that a bounded – in space and energy – mechanical system must typically have a recurrence property. That is, almost every (with the exception of a set of measure zero) initial state of an isolated, bounded, mechanical system will recur to within any specified accuracy, in the course of time. Of course, if H decreases over part of this motion, it must increase over some other part. This was referred to as *Zermelo's paradox.* The fact that this recurrence time may be much longer than the age of the universe is no escape from the argument that Boltzmann's derivation must contain some non-mechanical elements.

In fact, Boltzmann's derivation makes use of a stochastic argument called the *assumption of molecular chaos*, which allows an approximate calculation of the rates at which collisions are taking place in the gas. Nevertheless, as we discuss in later chapters, the derivation of the Boltzmann equation, the paradoxes surrounding it, and the modern ideas that have followed from it, are an essential part of nonequilibrium statistical mechanics, not only because of the deep and interesting conceptual problems involved, but also because the results of the Boltzmann equation are of great practical value in many areas of physics and engineering, and they need a firm foundation.

The recognition that the law of entropy increase must be something more than a consequence of Newton's laws led to the introduction of probabilistic ideas into this branch of physics. That is, the Boltzmann equation predicts things that are verified in laboratory experiments, despite the fact that this equation cannot be strictly correct; at least, not according to the laws of mechanics. One might say that the Boltzmann equation is 'probably' correct, rather than absolutely correct. It must describe a typical laboratory situation over times which are much longer than the time-scales of laboratory measurements. The H-theorem appears to hold for the typical behavior of a dilute gas, so the time-reversed motion of this gas, so important to Loschmidt, must correspond to a rare, very improbable, state of the gas. Moreover, the Poincaré recurrence time must be shown to be so large, compared to usual time-scales, that one will very likely never see such a recurrence. Since the reversal and recurrence objections are based entirely on mechanical principles, the introduction of probability arguments should be based upon the fact that macroscopic systems consist of large numbers of particles, and this fact should be coupled with a study of the dynamics of systems of large numbers of particles to provide a complete picture of irreversible processes.

The basic approach to the statistical mechanics of irreversible processes consists of three central themes:

1. One examines the average behavior of ensembles of mechanically identical systems. To do this, in classical mechanics at least, one constructs a phase-space, denoted Γ-space, with one coordinate axis for each canonical coordinate and one axis for each