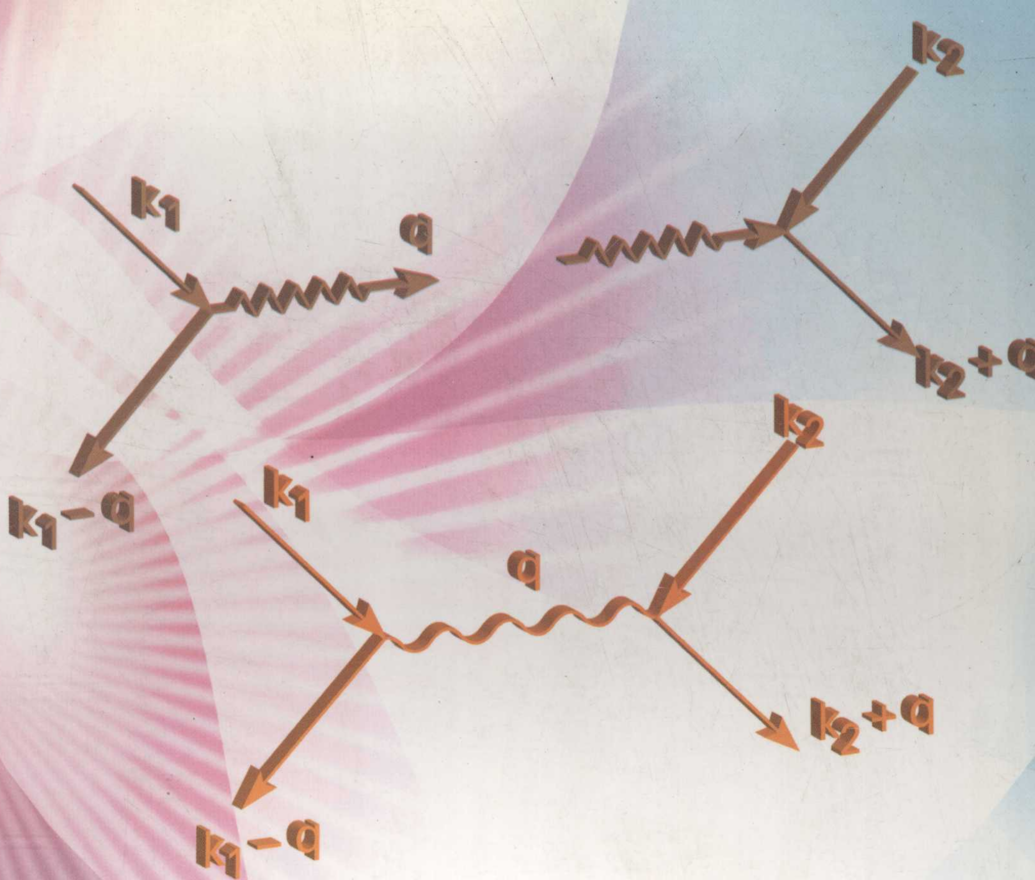
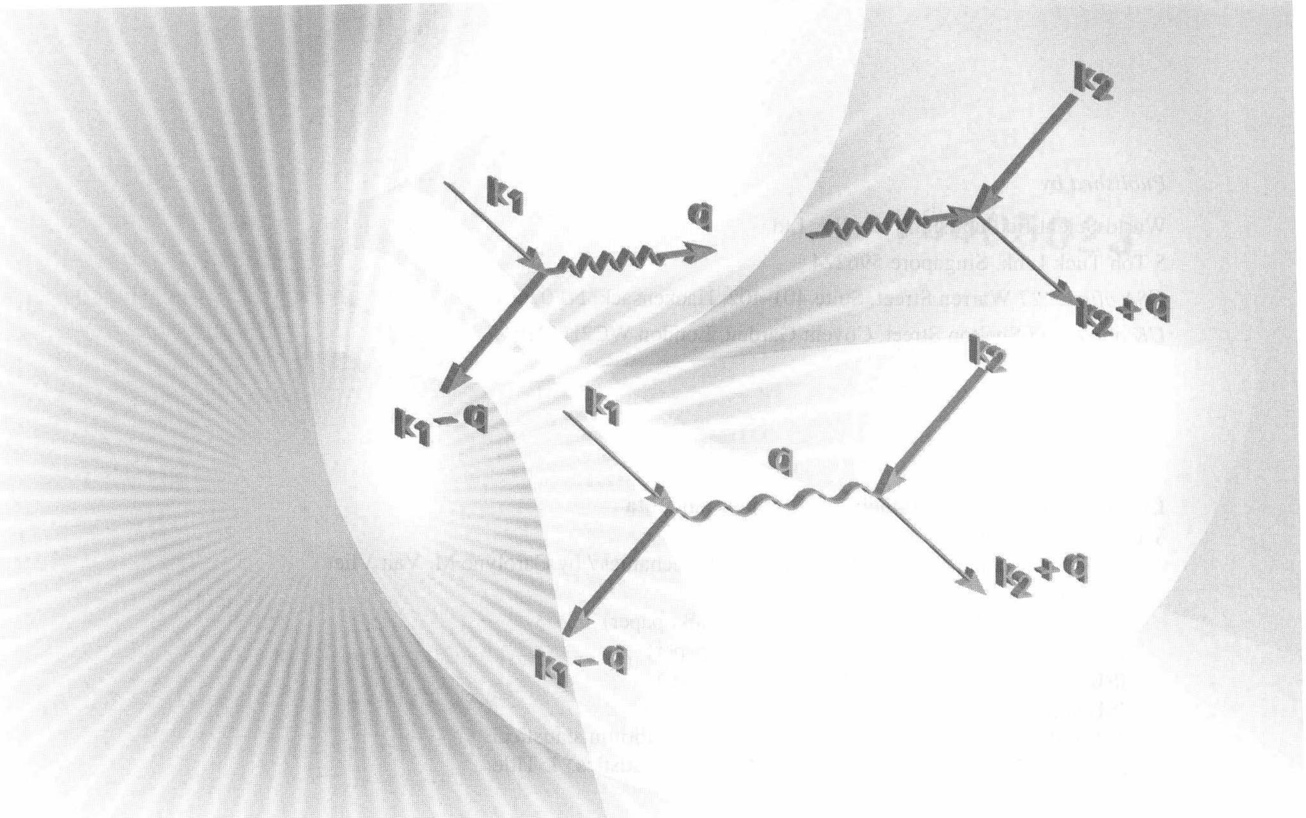


Equilibrium and Non-equilibrium Statistical Mechanics

Carolyne M. Van Vliet

World Scientific



Equilibrium and Non-equilibrium Statistical Mechanics

Carolyne M. Van Vliet

Professor Emerita of Theoretical Physics, Université de Montréal, Canada
and Adjunct Professor of Physics, University of Miami, USA

World Scientific

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

Library of Congress Cataloging-in-Publication Data
Van Vliet, Carolyne M.
Equilibrium and non-equilibrium statistical mechanics / by Carolyne M. Van Vliet.
p. cm.
ISBN-13: 978-981-270-477-1 (hardcover : alk. paper)
ISBN-10: 981-270-477-9 (hardcover : alk. paper)
ISBN-13: 978-981-270-478-8 (pbk. : alk. paper)
ISBN-10: 981-270-478-7 (pbk. : alk. paper)
1. Equilibrium--Statistical methods. 2. Nonequilibrium statistical mechanics. 3. Statistical mechanics. 4. Quantum statistics. I. Title.
QC174.86.E68V55 2008
530.13--dc22

2008002713

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Printed in Singapore by B & JO Enterprise

Preface

With statistical mechanics being one of the oldest branches of theoretical physics, going well back to the end of the nineteenth century, when the two great pioneers, Ludwig Boltzmann (1844-1906) in Graz, Munich and Vienna and J. Willard Gibbs (1839-1903) at Yale laid the foundations for the molecular approach to equilibrium and the statistical approach to many particle systems via ensemble theory, respectively, it seems a precarious task to endeavour to compose a textbook for a modern course in statistical physics, that will render homage to the past, summarise the exponential growth in the second half of the twentieth century – in particular with respect to critical phenomena in equilibrium statistical mechanics and the quantum foundations of transport processes and response theory in non-equilibrium statistical mechanics – to the student body of the twenty-first century, which typically has a two-semester slot in the graduate curriculum reserved for this topic. All this in contrast to electrodynamics and quantum mechanics, which is usually being taught in two rounds, each having two semesters available. While in these areas there is a rather common consensus about what should be taught, backed up by 'standard texts' in these fields – my own favourites being "Jackson" and "Messiah" – no such consensus exists with respect to statistical mechanics, usually named statistical physics these days, a pity, since the mechanical basis (classical or quantal) of the subject, as noticeable not only from the oeuvre of the pioneers mentioned above, but also stressed in little 'jewels' like Paul and Tatiana Ehrenfest's "The Conceptual Foundations of the Statistical Approach in Mechanics" (Leipzig, 1912, Cornell,1959) is often blatantly ignored. Instead, a great many modern texts commence with a résumé of macroscopic thermodynamics, after which a connection with the phase-space quantity $\ln\Omega$ is postulated and away we go. Needless to say that statistical mechanics is meant to provide the microscopic basis of all many-body systems, gases, liquids and condensed matter, of which the *ensuing* thermodynamic properties are established and form a basic part.

Yet, a text on statistical mechanics should not be just a text on many-body or condensed-matter physics, for which many excellent books are available; we mention e.g. Mahan's book "Many Particle Physics" of which an up-to-date third edition recently saw the light. While such books *use* statistical mechanics, part of which could be included in a statistical mechanics book as 'illustrations' of its principles, it is these principles which should be the expounded in a true text on the subject. The challenge to the writer is then how many illustrations or applications should be included. Obviously, the list is endless and a quick glance through half a dozen recent books reveals instantly the 'hobbies' of the authors.

This, then, brings me to my own views on what should be in a textbook on statistical mechanics, aimed at a two semester course. Given the fact that there is no *a priori* consensus the book should have sufficient material, so that a choice can be made as to what will be taught in a given year at a given place. Thus the book can have 900 pages, although only 600 or so can be taught. Even so, the foundations of the subject should not be undercut and more or less standard topics in equilibrium statistical mechanics, such as mean field theory, cluster and virial expansions, phase transitions, critical exponents, renormalization, quantum liquids, etc., to mention just a few, should be presented. In non-equilibrium material there is even less consensus, but most will agree that there should be an account of Boltzmann's H-theorem, classical transport theory and the hydrodynamic equations, the basis of quantum transport as contained in Pauli's and Van Hove's master equations, linear and nonlinear response theory, Brownian motion and other stochastic processes. For the rest the field is wide open and I have not hesitated to include my own preferences. Where I have been inspired by several textbooks, which I have from time to time recommended as reading material for my classes, I have made ample reference to these texts; however, I have always gone back to the original sources.

So let me present in this "à propos" a synopsis of my own evolution in this area. My course-packet at the Free University of Amsterdam included a full year in statistical mechanics, given by the late C.C. Jonker, who held 'the' chair in theoretical physics, as it was customary in those days; he certainly was overburdened and therefore took recourse to simply presenting the underground lectures in this area given in 1944 by his tutor, H.A. Kramers of the University of Leiden during World War II, when all university classes were suspended. They were excellent lectures! To our surprise these lectures were largely published in 1954 by D. ter Haar, who had also attended the underground lectures in 1944, in book-form: "Elements of Statistical Mechanics", (Rinehart & Co.) . Rightly he writes in his foreword, that "it is far from a platitude to say that it (the book) would never have been written but for Professor Kramers." My own pre-1954 lecture notes testify to this truth! In the mean time my research, which was concerned with fluctuation processes in semiconductors and photoconductors, turned more and more theoretical and I benefited for the theoretical part of my thesis from the scrutiny of one of Holland's most prominent theorists, the late Prof. H.B.G. Casimir; my interest in statistical mechanics was born.

In 1967 I had the pleasure to teach my first course in the field at the Physics Department of the University of Minnesota since my colleague Lewis Nosanov was on a sabbatical. He also introduced me to Van Hove's profound papers on the Pauli master equation and on the subject of irreversibility. The next spring I had the opportunity to discuss with Van Hove his so-called "diagonal singularity" in the perturbation expansion of the von Neumann equation, to which he attributed the irreversible character of the master equation, during a stay at the Theoretical Physics Institute at the University of Utrecht. These events shaped my thinking and I decided to forego my experimental endeavours. A brilliant opportunity opened up when I was offered a post in Physics at the Université de Montréal and as senior researcher at the Centre de Recherches Mathématiques (CRM). For many years I taught there courses in equilibrium and non-equilibrium statistical mechanics, and it is there that most ideas and presentations set forth in this book were developed. However, the usual conflict between teaching and writing research papers and proposals prevented me to condense my notes – several versions of which were made available for U. de M. students – to final book-form. That had to wait until after my second 'retirement', when I resumed among other topics graduate lectures in this field at the University of Miami. Needless to say, that many subjects had to be thoroughly updated or added. Nevertheless, the reader will find much of the flavour of my original lectures in this text and I tend to believe that this text still reflects more than the usual book that my origins in this field go back to Kramers and through him to the founders. So the reader will find here Gibbs' original considerations about entropy in the microcanonical ensemble, adapted, however, to quantum systems, not found in any present-day text. For the H-theorem, extended to quantum systems, I have freely borrowed from Tolman and passages of several older books, like Fowler and Fowler-Guggenheim, where still relevant, have been included. In the early days of my studies I profited much from Sommerfeld's book on the topic (Vol. 5 of his series on Theoretical Physics) and from Schrödinger's little but revealing book on "Statistical Thermodynamics", which used and explained in detail the Darwin-Fowler procedure to obtain the Boltzmann, Bose-Einstein and Fermi-Dirac distributions, all based on the microcanonical ensemble, which is the only ensemble that connects directly to classical mechanics via Poincaré invariants and Liouville's equation of 1838. Yet the emphasis in this book is on quantum statistics, and a replacement of the phase space by the appropriate Hilbert space is found on the earliest pages. Later on the Fock space and the occupation-number formalism, commonly called the second quantization procedure, is introduced, given that many-body Hamiltonians of strongly interacting particles can only properly be described with creation and annihilation operators. Since the typical student who takes a course in statistical physics has not yet had an exposure to advanced quantum courses or quantum-field theory, these developments are set forth in detail. For its introduction I still find Dirac's book, fourth edition (1958) one of the best sources.

This brings me to the organization of this text. Both the division on equilibrium statistical mechanics and on non-equilibrium statistical mechanics have three main parts each, A-C and D-F, respectively. Part A deals with the general principles of many-particle systems. There are five chapters, the first one of which is of an introductory nature, dealing with the purpose of statistical mechanics, my philosophy on the subject and a bit of thermodynamics, whereby we emphasize the fact that Gibbs' point of departure basically (may) conflict(s) with the standard views cherished in macroscopic thermodynamics, as set forth for example in Callen's book on the subject. We introduce classical and quantum ensembles, the *a*-space for 'mesoscopic' variables as found with van Kampen and in the classical text on non-equilibrium thermodynamics by de Groot and Mazur and other places, with emphasis on the microcanonical ensemble. Also, elementary and not-so-elementary topics in probability theory are discussed: transforms, generating functions, cumulants, etc. In Chapter II we thoroughly discuss the statistics of closed systems and in chapter III we deal with thermodynamics *a posteriori*, i.e., as a consequence of Gibbs' approach to the microcanonical ensemble, leading to the basic result $S = k \ln \Delta\Gamma$, where S is the entropy and $\Delta\Gamma$ is the accessible number of quantum states or the microcanonical partition function. The rest of needed thermodynamics then follows now as a desert, rather than as usual in the introductory part of a text. We then connect with Boltzmann's ideas and the famous relationship $S = k \log W$, as well as Einstein's inversion thereof. Next in Chapter IV we introduce the more common and useful ensembles, the canonical and grand-canonical ensemble. In order to avoid that all this formalism becomes sterile we liven up the story at this point with realistic applications of these ensembles and we embark on a variety of simple as well as quite complex topics, including the 1D Ising model, the 1D hard-core model of Tonk and Takahashi, dense classical gases involving cluster-integral diagrams, the cumulant expansion and the virial expansion. To do justice to my heritage I have also included the essence of Ornstein's Ph.D. thesis on the derivation of van der Waals' equation and van Kampen's later elaboration. The usual mean-field theories are discussed, including the Weiss molecular field and the Debye-Hückel theory for ionized gases. In the next chapter we make a little excursion into generalized canonical ensembles and transformation theory, as e.g. found in Münster's book; this concludes part A.

In the next part, B, we mainly consider perfect gases and their properties. The level of difficulty here, initially, is a great step backwards. So be it! It is like the mid-January thaw that usually appears to cheer up the long winters in Montreal. However, apart from the elementary (non-existing) Boltzmann gas, we soon go over to quantum gases and it is here that second quantization is set forth and elaborated. We discuss Bose-Einstein condensation and the elementary excitations in solids, phonons and electron-phonon interaction. Part C then contains the most pertinent theory of modern statistical mechanics, involving quantum systems with strong interactions, for which a quantum-field formulation is indispensable. We discuss critical phenomena and phase transitions, renormalization, the 2D Ising model, quantum liquids, the basis of superconductivity, etc. A part with the diagrammatic approach to many-body theory has been added for the more advanced student. Clearly, to do justice to all the developments of the second half of the twentieth century, for which the names of Wilson, Fisher, Widom, Kadanoff, Stanley, and many others, stand out, a book of several thousand pages would not suffice. So we have made a choice – our choice – constantly mindful of Goethe's words: *"in der Beschränkung zeigt sich der Meister."*

Now some words regarding the second division. We begin non-equilibrium statistical mechanics with what we call "Boltzmann theory", part D, with the developments including, however, quantum gases viewed from a semi-classical point of view. We prove the H-theorem for Boltzmann, B-E and F-D gases. We then discuss the hydrodynamic equations, near-equilibrium classical transport involving electrical and thermal conductivity problems, and (a novum perhaps) transport far from equilibrium, based on the papers of Yamashita and Watanabe, culminating in the Davydov and Druyvesteyn distributions for hot plasmas and hot electron gases. In the next part, E, we return to serious quantum developments and we establish the basis for quantum non-equilibrium irreversible kinetic equations, following the work of Van Hove, Zwanzig, Fano , Kubo, Mori and others. Also, we discuss linear and nonlinear response theory, the Wigner formalism and many applications. This material is based in part on articles by the author and I gratefully acknowledge the help and papers of my former graduate students and present colleagues P. Vasilopoulos, M. Charbonneau and A. Barrios. A special section has been devoted to the meagre foundations of linear response theory, discussed by van Kampen in his well-known Physica Norvegica paper, and cleared up, or at least elucidated I hope, in my response in a 1988 paper in the J. of Statistical Physics.

Lastly, part F deals with stochastic processes. I have started with the older ideas on Brownian motion by Einstein, Smoluwkowski, Kramers, Moyal, and of the Dutch School with the standard papers of Ornstein and Burger, Uhlenbeck and Ornstein, Chandrasekhar and others. A short sub-chapter is devoted to spectral analysis and besides the Wiener–Khintchine theorem, the methods of the 'short-time average' (MacDonald, Milatz), of 'elementary events' (Campbell, Carson) and the Allen-variance theorem, suitable for many forms of 'pathological noise', do the round. A single section is devoted to fluctuation processes in solids, to which I have actively contributed for many years, but, mostly, referral to the literature must suffice. A further chapter is devoted to continuous stochastic processes and branching processes and finally there is brief chapter on fluctuations in radiation fields and photons, based on work by Glauber, Sudarshan, Louisell and others with experimental verification by Zijlstra's group on counting statistics in Utrecht. We understand that the usual curriculum leaves no time for stochastic processes but for the barest principles of diffusion and Brownian motion, but we feel that stochastic processes, when microscopically founded as in this text, are an essential part of non-equilibrium statistical mechanics. Perhaps much of it can be relegated to a special seminar.

Several important topics have not been treated. We mention disordered systems and percolation theory in equilibrium statistical mechanics and out-of-equilibrium phase transitions in non-equilibrium theory; we must refer the reader to other texts.

A note on units, quite inconsequential in statistical mechanics, is in order. With rare exceptions we employ rationalized Gaussian or Heaviside–Lorentz units. The integrity of electromagnetic theory is then maintained, but the equations 'look like' as in the *Système International*; the *S-I* proponent only has to stick in ε_0 and μ_0 at appropriate places and remove some 'c's.

Problems have been added at the end of each chapter. They are generally of two kinds. First, there are exercises to verify some not explicitly derived results as well as straightforward applications. Secondly there are extensions of the theory for which space lacked in the chapter proper; the problems are an integral part of the text.

Finally, I have of course a list of acknowledgements. First of all, I thank the many graduate students who took my courses. If in earlier times I have not given enough information on certain topics, my hope remains that I have at least been able to awaken their critical faculties and their interest in this field. I also thank all who have pointed out errors and who have made known their wishes for improvements.

Since by nature I am more stimulated by auditory than visual inputs, I have greatly benefited from lectures, colloquia, and presentations at symposia and by the many visitors received yearly at the CRM. In particular stand out the lectures by the titulaires of the Chaire André Aisenstadt at the Université de Montréal, notably by the late Professors Sybren de Groot and Marc Kac. Also, by the visitors Profs. L. de Sobrino of UBC, S. Fujita of SUNY at Buffalo, Ch. G. van Weert and A.J. Kox of the Institute for Theoretical Physics at the University of Amsterdam and many others. I vividly remember and acknowledge the presentation by (and subsequent discussions with) Prof. E.G.D. Cohen of Rockefeller University in honour of Prof. van Kampen's sixtieth birthday at the University of Utrecht. I thank Prof. van Kampen for many discussions over the years regarding linear response theory and the assumptions underlying the master equation. And last but not least, I have learned much at the bi-annual conferences organized by Prof. Joel Lebowitz at Yeshiva University and later at Rutgers University.

A final word of thanks goes to Professor George Alexandrakis, former Chairman of the Physics Department of the University of Miami, who welcomed me as an Adjunct Professor in the department in 2001. I also thank many colleagues in Miami for discussions, seminars, and their impact; in particular Profs. M. Huerta, J. Nearing, O. Alvarez, H. Gordon, J. Ashkenazi and F. Zuo. Special thanks are due to Dr. A. Barrios, Mr. P. Sajnani and to Prof. Olga Korotkova for their critical reading of various chapters of the Non-equilibrium Part of this text.

Being myself illiterate in computers in the eighties and early nineties, I must acknowledge the earlier versions of parts of this text, which were ably composed in Tex or AmTex by Mme Louise Letendre of the CRM. The present version of this text being sent to the publisher was composed by myself in MS WORD 2003 and Math-type 5.2c. I am greatly indebted to the Production Manager Ms. Yolande Koh of WSPC and our Computer Scientist Mr. Marco Monti for their valuable advice.

Miami, Fall 2007

Contents

NON-EQUILIBRIUM STATISTISTICAL MECHANICS

PART D. CLASSICAL TRANSPORT THEORY