Quantum Theory of Collective Phenomena

G. L. SEWELL

Quantum Theory of Collective Phenomena

G. L. SEWELL
Department of Physics, Queen Mary College, London

CLARENDON PRESS • OXFORD
1986

Oxford University Press, Walton Street, Oxford OX2 6DP

Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Kuala Lumpur Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland
and associated companies in
Beirut Berlin Ibadan Nicosia

Oxford is a trade mark of Oxford University Press

Published in the United States
by Oxford University Press, New York

British Library Cataloguing in Publication Data
Sewell, G. L.
Quantum theory of collective phenomena.——
(*Monographs on the physics and chemistry of materials*)
1. *Statistical mechanics* 2. *Quantum field theory*
I. Title II. Series
530.1'33 *QC*174.45

ISBN 0-19-851371-2

Library of Congress Cataloging in Publication Data
Sewell, G. L.
Quantum theory of collective phenomena.
(*Monographs on the physics and chemistry of materials*)
Bibliography: p. -
Includes index.
1. *Quantum theory.* 2. *Statistical thermodynamics.*
3. *Phase transformations* (*Statistical physics*)
I. Title. II. Title: Collective phenomena
*QC*174.12.*S*48 1985 530.1'2 85-15522
ISBN 0-19-851371-2

Typeset and Printed in Northern Ireland by
The Universities Press (Belfast) Ltd

Preface

The macroscopic properties of matter are governed by quantum mechanical processes that are collective, in that they involve the co-operation of enormous numbers of particles. Correspondingly, the quantum theory of macroscopic phenomena requires concepts, such as those of order and entropy, that represent collective effects in 'very large' assemblies of particles. It is therefore radically different from the quantum theory of atoms and small molecules, where such concepts have no relevance.

Important developments in the quantum theory of macroscopic, or collective, phenomena have ensued from the discovery that the idealization of many-particle systems as infinite can reveal some of their intrinsic properties that would otherwise be masked by finite-size effects. The essential reason for this may be traced to the fact that this idealization permits qualitative distinctions between the descriptions of matter at the macroscopic and microscopic, or global and local, levels, whereas the corresponding distinctions for finite systems are merely quantitative. Thus, for example, an infinite system, unlike a finite one, admits inequivalent representations of its observables, corresponding to macroscopically different classes of states, such as those belonging to different thermodynamic phases. Consequently, it emerges that the model of an infinite system provides the conceptual structure needed for a theory of phase transitions, characterized by spontaneous symmetry changes as well as thermodynamical singularities. It also provides the framework for theories of irreversible processes, free from Poincaré cycles, and metastable states, characterized by stability of a lower grade than that of thermal equilibrium.

The object of this book is to provide a systematic approach to the quantum theory of collective phenomena, based principally on the model of infinite systems. The book is addressed to physicists and chemists who are interested in understanding the scope of this approach, and also to mathematicians who may wish to study the structure and physical relevance of the model. Throughout the book, I have aimed to keep the mathematics as simple as possible, without sacrificing rigour. The book is thus designed to be readable on the basis of a knowledge of standard quantum theory and statistical mechanics, and of the essentials of mathematical analysis and vector space theory. Any additional mathematics required here, mainly elementary functional analysis, will be expounded in self-contained form, either in the main text or in the Appendices: for example, an Appendix to Chapter 2 is devoted to an exposition of the elements of Hilbert space theory.

The book consists of three parts. Part I is an exposition of the generalized form of quantum theory of both finite and infinite systems. Part II consists of a general formulation of statistical thermodynamics within the framework of Part I. This contains what I believe to be a new derivation of thermodynamics with phase structure (in Chapter 4), which has been obtained by incorporating conserved global observables into the model of infinite systems. Part III provides a treatment of the phenomena of phase transitions, metastability and the generation of ordered structures far from equilibrium, within the framework of Parts I and II. This serves to co-ordinate the theory of these phenomena, placing the results obtained by various methods in a general scheme. It will be seen that, while some of these results can be obtained by traditional methods, there are also some whose very conception requires the idealization of infinite systems.

Since a number of the topics treated in this book are enormous subjects in themselves, I have had to be highly selective in my choice of material. The choice made here, while inevitably dependent upon my own interests, has been governed by the aim of providing a coherent and relatively simple approach to the theory of collective phenomena.

London G. L. S.
January 1985

Acknowledgements

It is a great pleasure to thank Professor H. Fröhlich, Editor of this series of monographs, for inviting me to write this book and for various constructive suggestions and criticisms during its preparation. I am also grateful to Professor O. Penrose for some very useful criticisms of a preliminary draft of the first part of the book. Finally, I would like to thank Mrs. M. Puplett for her patience and efficiency in typing the manuscript.

Contents

Part I

The generalized quantum mechanical framework

1

Introductory discussion on the quantum theory of macroscopic systems

Macroscopic systems enjoy properties that are qualitatively different from those of atoms and molecules, despite the fact that they are composed of the same basic constituents, namely nuclei and electrons. For example, they exhibit phenomena such as phase transitions, dissipative processes, and even biological growth, that do not occur in the atomic world. Evidently, such phenomena must be, in some sense, *collective*,† in that they involve the cooperation of enormous numbers of particles: for otherwise the properties of macroscopic systems would essentially reduce to those of independent atoms and molecules.

The problem of how macroscopic phenomena arise from the properties of the microscopic constituents of matter is basically a quantum mechanical one. That quantum, rather than classical, mechanics is essential here is evident from the great wealth of phenomena in which quantum effects operate on the macroscopic scale. For example, the Third Law of Thermodynamics is a quantum law, the stability of matter‡ itself is a quantum phenomenon; while the physical processes of Josephson tunnelling§ and laser radiation,¶ as well as certain biological ones,|| are characterized in terms of 'macroscopic wave-functions' of a purely quantum nature.

The quantum theory of macroscopic systems is designed to provide a model relating the bulk properties of matter to the microscopic ones of its constituent particles. Since such a model must possess the structure needed to accommodate a description of collective phenomena, characteristic of macroscopic systems only, it is evident that it must contain concepts that are *qualitatively* different from those of atomic physics.

In order to see the nature of the problems involved here, we start by noting that a macroscopic system is composed of an enormous number, e.g. 10^{24}, of interacting particles of one, or possibly several, species. At a microscopic level, therefore, its properties are governed by the Schrödinger equation for this assembly of particles. However, in view of the huge

† The idea of collective behaviour of many-particle systems was first explicitly introduced by Bohm and Pines (1951).

‡ See Dyson and Lenard (1967, 1968); Lieb and Thirring (1975); Lieb (1976).

§ See Josephson (1964).

¶ See Graham and Haken (1970).

|| See H. Fröhlich (1969).

number of particles in the system, this equation is fantastically complicated: indeed its extreme complexity represents an essential part of the physical situation, being closely connected with the 'molecular chaos' that is basic to statistical mechanics. It is this complexity that makes the many-body problem of extracting physically relevant information from the Schrödinger equation radically different from anything encountered in atomic physics. For, as cogently argued by H. Fröhlich (1967, 1973), it imposes a situation where detailed solution of the Schrödinger equation would be too complex to even be contemplated† and where, consequently, the essential role of this equation in the many-body problem is that of a key to interrelationships between appropriate macroscopic variables, as in thermodynamics or hydrodynamics. This signifies that the many-body problem should be cast, *ab initio*, in both *macroscopic and microscopic* terms. One can also see this from the empirical fact that the phenomenological properties of a macroscopic many-particle system are determined not only by its microscopic constitution, but also by its thermodynamic phase or, more generally, by the macroscopic constraints imposed on it: for example, a system in the solid phase lacks the hydrodynamical properties of a liquid.

What is needed, then, is a quantum mechanical model that admits precise mathematical description in both macroscopic and microscopic terms. As a prerequisite for this, we require clear-cut characterizations of macroscopic systems and variables, and this poses a problem, since it is not a priori evident how large an assembly of particles must be before it can be considered to be macroscopic. However, an essential clue to the characterization of macroscopicality is that, at an empirical level, the hallmark of macroscopic objects is that their intensive properties, e.g. their equations of state, are independent of their sizes. This indicates that the intensive properties of an assembly of particles of a given species tend to definite limits when the number of particles tends to infinity at constant density; and that a real macroscopic system of these particles is one that is sufficiently large for its intensive properties to be experimentally indistinguishable from these limiting ones. Furthermore, at the statistical mechanical level, it has been proved‡ that intensive properties of many-particle systems do indeed converge to definite limits, as their sizes tend to infinity, under very general conditions on their interactions.§

These considerations lead naturally to a model, in which a macroscopic system is *idealized* as an infinite assembly of particles, whose density is

† This is not merely a technical point since, even if one could solve the Schrödinger equation with the aid of a supercomputer, its solution would surely be so complicated as to be unintelligible; and the problem of extracting physically relevant information from it would presumably be no simpler than the original one.

‡ See Ruelle's book (1969*a*).

§ These conditions exclude gravitational systems, whose large-scale limiting properties are of a different nature (cf. Hertel and Thirring 1971).

finite. It emerges that this model, which has been extensively studied† in the last two decades, possesses just the structures needed for a theory of collective phenomena, exposing in sharp relief certain intrinsic properties of matter that would otherwise be masked by finite-size effects. The model is defined (cf. Chapter 2) so that its observables and states reduce, in each bounded region, to those of a corresponding finite system of particles there; while its dynamics and intensive thermodynamic potentials are defined as infinite volume limits of those of a finite system of particles of the given species. Thus, the model is constructed as an infinite volume limit of that of a large, but finite, system of the given species of particles.

Let us now briefly indicate how this model provides the natural setting for a systematic theory of collective phenomena. Turning first to the thermodynamic properties of matter, the passage to the infinite volume limit serves to simplify the forms of the thermodynamic potentials by eliminating contributions, due to surface and other finite-size effects, whose extreme smallness, in real macroscopic systems, is concealed by the complexity of their mathematical forms. In particular, it leads to a very important gain for the theory of phase transitions. For, whereas the thermodynamic potentials of a finite system are perfectly smooth,‡ their infinite volume limits can possess singularities, and are known to do so for various models § Thus, it is only by passing to the infinite volume limit that one can characterize phase transitions by singularities in the thermodynamic potentials. Here, we emphasize that the passage to this limit does not introduce anything spurious into the theory, but simply sharpens huge gradients into the forms of singularities, which they simulate so closely as to be experimentally indistinguishable from them. From a theoretical standpoint, this constitutes a great conceptual and methodological gain, since singularities may be revealed by certain qualitative features of a model, whereas the detection of huge gradients requires detailed computations that may be too complicated to be either feasible or enlightening.

The model of an infinite system also introduces physically relevant new structures into the theory of both equilibrium and non-equilibrium properties of matter, that go far beyond thermodynamics. A key to these structures is the fact that the model admits a clear-cut distinction between local and global variables, the former referring to the bounded spatial regions of the system and the latter to the whole of it. It therefore permits the natural step of designating as *macroscopic* variables the global intensive quantities given by space-averages of local observables – examples of these are the densities of mass and of energy of the system. Furthermore, these

† See, for example, the books by Ruelle (1969*a*), Emch (1972), Dubin (1974), Bratteli and Robinson (1979, 1981), and Thirring (1980).

‡ See Lebowitz (1968).

§ A useful general reference to models with phase transitions is provided by various articles in the book by Domb and Green (1972).

variables may be used to classify the states of the model with respect to their macroscopic properties in a way that would not be possible for finite systems. For the observables of an infinite system generally have an infinity of inequivalent representations,† each corresponding to a class of macroscopically equivalent but microscopically different states, whereas the observables of a finite system have but one‡ irreducible representation. Hence, a state of an infinite system may be defined macroscopically by a representation and microscopically by a vector or density matrix in the representation space.

Thus, the model possesses sufficient structure to admit description in the macroscopic and microscopic terms needed for a theory of collective phenomena. In the following chapters, we shall show how it may be employed to obtain a general derivation of thermodynamics with phase structure (Chapter 4) and to provide the framework for theories of phase transitions, irreversibility, and metastability. In particular, we shall see that it admits theories of phase transitions, characterized not only by thermodynamical singularities, but also by symmetry breakdown corresponding to a certain 'macroscopic degeneracy' (Chapters 2–5); of critical phenomena (Chapter 5); of metastable states, characterized by a limited stability of a local, rather than global, kind (Chapters 3, 6); of irreversible processes, free from Poincaré cycles (Chapter 7); and of the generation of ordered structures, far from equilibrium, by such processes (Chapter 7).

† A simple demonstration of this is given in Chapter 2 (§2.3). For a general treatment, see Emch's book (1972) and references given there.

‡ See Von Neumann (1931).