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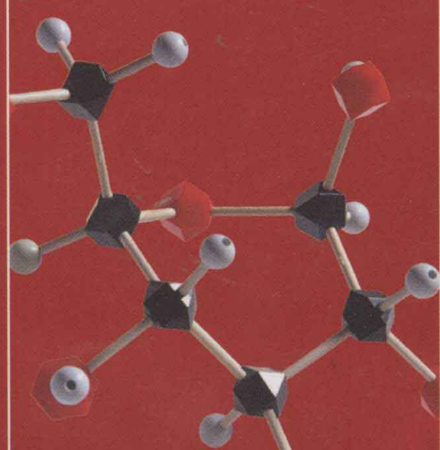
Superconductivity, Superfluids and Condensates

超导、超流和凝聚体



J. F. Annett

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Preface

Ever since their original discovery nearly 100 years ago, superconductors and superfluids have led to an incredible number of unexpected and surprising new phenomena. The theories which eventually explained superconductivity in metals and superfluid ^{4}He count among the greatest achievements in theoretical many-body physics, and have had profound implications in many other areas, such as in the construction of the "Higgs mechanism" and the standard model of particle physics.

Even now there is no sign that the pace of progress is slowing down. Indeed recent years have seen renewed interest in the field in following the 1986 discovery of cuprate high temperature superconductivity and the 1995 announcement of Bose–Einstein condensation (BEC) in ultra-cold atomic gases. These breakthroughs have tremendously widened the scope of the area of "low temperature physics" from 165 K (only about $-100°$C, a cold day at the North Pole) the highest confirmed superconducting transition temperature ever recorded, to the realm of nano-Kelvin in laser trapped condensates of atomic gases. Furthermore an incredibly wide range of materials is now known to be superconducting. The field is no longer confined to the study of the metallic elements and their alloys, but now includes the study of complex oxides, carbon-based materials (such as fullerene C_{60}), organic conductors, rare earth based compounds (heavy fermion materials), and materials based on sulphur and boron (MgB_2 superconductivity was discovered in 2001). Commercial applications of superconducting technology are also increasing, albeit slowly. The LHC ring currently (in 2003) being installed at the CERN particle physics center is possible only because of considerable recent advances in superconducting magnet technology. But even this uses "traditional" superconducting materials. In principle, even more powerful magnets could be built using novel high temperature superconducting materials, although these materials are difficult to work with and there are many technical problems still to be overcome.

The goal of this book is to provide a clear and concise first introduction to this subject. It is primarily intended for use by final year undergraduates and beginning postgraduates, whether in physics, chemistry, or materials science departments. Hopefully experienced scientists and others will also find it interesting and useful.

For the student, the concepts involved in superfluidity and superconductivity can be difficult subject to master. It requires the use of many different elements from thermodynamics, electromagnetism, quantum mechanics, and solid state physics. Theories of superconductivity, such as the Bardeen Cooper Schrieffer (BCS) theory, are also most naturally written in the mathematics of quantum field theory, a subject which is well beyond the usual undergraduate physics curriculum. This book attempts to minimize the use of these advanced mathematical techniques so as to make the subject more accessible to beginners.

Of course, those intending to study superconductivity at a more advanced level will need to go on to the more advanced books. But I believe most of the key concepts are fully understandable using standard undergraduate level quantum mechanics, statistical physics, and some solid state physics. Among the other books in the **Oxford Master Series in Condensed Matter**, the volumes *Band theory and electronic properties of solids* by John Singleton (2001), and *Magnetism in condensed matter* by Stephen Blundell (2001) contain the most relevant background material. This book assumes an initial knowledge of solid state physics at this level, and builds upon this (or equivalent level) foundation.

Of course, there are also many other books about superconductivity and superfluids. Indeed each chapter of this book contains suggestions for further reading and references to some of the excellent books and review articles that have been written about superconductivity. However, unlike many of these earlier books, this book is not intended to be a fully comprehensive reference, but merely an introduction. Also, by combinining superconductivity, superfluids and BEC within a single text, it is hoped to emphasize the many strong links and similarities between these very different physical systems. Modern topics, such as unconventional superconductivity, are also essential for students studying superconductivity nowadays and are introduced in this book.

The basic framework of the earlier chapters derives from lecture courses I have given in Bristol and at a number of summer and winter schools elsewhere over the past few years. The first three chapters introduce the key experimental facts and the basic theoretical framework. First, Chapter 1 introduces BEC and its experimental realization in ultra-cold atomic gases. The next chapter introduces superfluid ^{4}He and Chapter 3 discusses the basic phenomena of superconductivity. These chapters can be understood by anyone with a basic understanding of undergraduate solid state physics, quantum mechanics, electromagnetism, and thermodynamics. Chapter 4 develops the theory of superconductivity using the phenomenological Ginzburg–Landau theory developed by the Landau school in Moscow during the 1950s. This theory is still very useful today, since it is mathematically elegant and can describe many complex phenomena (such as the Abrikosov vortex lattice) within a simple and powerful framework. The next two chapters introduce the BCS theory of superconductivity. In order to keep the level accessible to undergraduates I have attempted to minimize the use of the mathematical machinery of quantum field theory, although inevitably some key concepts, such as Feynman diagrams, are necessary. The effort is split into two parts: Chapter 5 introducing the language of coherent states and quantum field operators, while Chapter 6 develops the BCS theory itself. These two chapters should be self-contained so that they are comprehensible whether or not the reader has had prior experience in quantum field theory techniques. The final chapter of the book covers some more specialized, but still very important, topics. The fascinating properties of superfluid ^{3}He are described in Chapter 7. This chapter also introduces unconventional Cooper pairing and is based on a series of review articles in which I discussed the evidence for or against unconventional pairing in the high temperature superconductors.

For a teacher considering this book for an undergraduate or graduate level course, it can be used in many ways depending on the appropriate level for the students. Rather than just starting at Chapter 1 and progressing in linear fashion, one could start at Chapter 3 to concentrate on the superconductivity parts alone. Chapters 3–6 would provide a sound introduction to superconductivity up to the level of the BCS theory. On the other hand, for a graduate level course one could start with Chapters 4 or 5 to get immediately to the many-body physics aspects. Chapter 7 could be considered to be research level or for specialists only, but on the other hand could be read as stand-alone reference by students or researchers wanting to get a quick background knowledge of superfluid ^{3}He or unconventional superconductivity.

The book does not attempt to cover comprehensively all areas of modern superconductivity. The more mathematically involved elements of BCS and other theories have been omitted. Several more advanced and comprehensive books exist, which have good coverage at a much more detailed level. To really master the BCS theory fully one should first learn the full language of many-particle quantum field theory. Topics relating to the applications of superconductivity are also only covered briefly in this book, but again there are more specialized books available.

Finally, I would like to dedicate this book to my friends, mentors, and colleagues who, over the years, have shown me how fascinating the world of condensed matter physics can be. These include Roger Haydock, Volker Heine, Richard Martin, Nigel Goldenfeld, Tony Leggett, Balazs Györffy, and many others too numerous to mention.

James F. Annett[1]
University of Bristol, March 2003

[1] I will be happy to receive any comments and corrections on this book by Email to james.annett@bristol.ac.uk

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1.1 Introduction

Superconductivity, **superfluidity**, and **Bose–Einstein condensation** (BEC) are among the most fascinating phenomena in nature. Their strange and often surprising properties are direct consequences of quantum mechanics. This is why they only occur at low temperatures, and it is very difficult (but hopefully not impossible!) to find a room temperature superconductor. But, while most other quantum effects only appear in matter on the atomic or subatomic scale, superfluids and superconductors show the effects of quantum mechanics acting on the bulk properties of matter on a large scale. In essence they are **macroscopic quantum phenomena**.

In this book we shall discuss the three different types of macroscopic quantum states: superconductors, superfluids, and atomic Bose–Einstein condensates. As we shall see, these have a great deal in common with each other and can be described by similar theoretical ideas. The key discoveries have taken place over nearly a hundred years. Table 1.1 lists some of the key discoveries, starting in the early years of the twentieth century and still continuing rapidly today. The field of low temperature physics can be said to have its beginnings in 1908, where helium was first liquified at the laboratory of H. Kammerling Onnes in Leiden, The Netherlands. Very soon afterwards, superconductivity was discovered in the same laboratory. But the theory of superconductivity was not fully developed for until nearly forty years later, with the advent of the

Table 1.1 Some of the key discoveries in the history of superconductivity, superfluidity, and BEC

1908	Liquefaction of ^{4}He at 4.2 K
1911	Superconductivity discovered in Hg at 4.1 K
1925	Bose–Einstein condensation (BEC) predicted
1927	λ transition found in ^{4}He at 2.2 K
1933	Meissner–Ochsenfeld effect observed
1938	Demonstration of superfluidity in ^{4}He
1950	Ginzburg–Landau theory of superconductivity
1957	Bardeen Cooper Schrieffer (BCS) theory
1957	Abrikosov flux lattice
1962	Josephson effect
1963–4	Anderson–Higgs mechanism
1971	Superfluidity found in ^{3}He at 2.8 mK
1986	High temperature superconductivity discovered, 30–165 K
1995	BEC achieved in atomic gases, 0.5 μK

Bardeen Cooper Schrieffer (BCS) theory.[1] In the case of BEC it was the theory that came first, in the 1920s, while BEC was only finally realized experimentally as recently as 1995.

Despite this long history, research in these states of matter is still developing rapidly, and has been revolutionized with new discoveries in recent years. At one extreme we have a gradual progression to systems at lower and lower temperatures. Atomic BEC are now produced and studied at temperatures of nano-Kelvin. On the other hand high temperature superconductors have been discovered, which show superconductivity at much higher temperatures than had been previously believed possible. Currently the highest confirmed superconducting transition temperature, T_c, at room pressure is about 133 K, in the compound $HgBa_2Ca_2Cu_3O_{8+\delta}$. This transition temperature can be raised to a maximum of about 164 K when the material is subjected to high pressures of order 30 GPa, currently the highest confirmed value of T_c for any superconducting material. Superconductivity at such high temperatures almost certainly cannot be explained within the normal BCS theory of superconductivity, and the search for a new theory of superconductivity which can explain these remarkable materials is still one of the central unsolved problems of modern physics.

This book is organized as follows. In this chapter we start with the simplest of these three macroscopic quantum states, BEC. We shall first review the concept of a BEC, and then see how it was finally possible to realize this state experimentally in ultra-cold atomic gases using the modern techniques of laser cooling and trapping of atoms. The following two chapters introduce the basic phenomena associated with superfluidity and superconductivity. Chapters 4–6 develop the theories of these macroscopic quantum states, leading up to the full BCS theory. The final chapter goes into some more specialized areas: superfluidity in ^{3}He and superconductors with unconventional Cooper pairing.

[1] Some offshoots of the development of superconductivity have had quite unexpected consequences in other fields of physics. The **Josephson effect** leads to a standard relationship between voltage, V, and frequency, ν: $V = (h/2e)\nu$, where h is Planck's constant and e is the electron charge. This provides the most accurate known method of measuring the combination of fundamental constants h/e and is used to determine the best values of these constants. A second surprising discovery listed in Table 1.1 is the **Anderson–Higgs mechanism**. Philip Anderson explained the expulsion of magnetic flux from superconductors in terms of *spontaneous breaking of gauge symmetry*. Applying essentially the same idea to elementary particle physics Peter Higgs was able to explain the origin of mass of elementary particles. The search for the related *Higgs boson* continues today at large accelerators such as CERN and Fermilab.

1.2 Bose–Einstein statistics

In 1924 the Indian physicist S.N. Bose wrote to Einstein describing a new method to derive the Plank black-body radiation formula. At that time Einstein was already world-famous and had just won the Nobel prize for his quantum mechanical explanation of the photoelectric effect. Bose was a relatively unknown scientist working in Dacca (now Bangladesh), and his earlier letters to European journals had been ignored. But Einstein was impressed by the novel ideas in Bose's letter, and helped him to publish the results.[2] The new idea was to treat the electromagnetic waves of the black-body as a gas of **identical particles**. For the first time, this showed that the mysterious light quanta, introduced by Planck in 1900 and used by Einstein in his 1905 explanation of the photo-electric effect, could actually be thought of as particles of light, that is, what we now call photons. Einstein soon saw that the same method could be used not only for light, but also for an ideal gas of particles with mass. This was the first proper quantum mechanical generalization of the standard classical theory of the ideal gas developed by Boltzmann, Maxwell, and Gibbs. We know now that there are two distinct quantum ideal gases, corresponding to either Bose–Einstein or Fermi–Dirac statistics. The method of counting quantum states introduced by Bose and Einstein applies to **boson** particles, such as photons or ^{4}He atoms.

[2] For some more historical details see "The man who chopped up light" (Home and Griffin 1994).

The key idea is that for identical quantum particles, we can simply count the number of available quantum states using combinatorics. If we have N_s identical bose particles in M_s available quantum states then there are

$$W_s = \frac{(N_s + M_s - 1)!}{N_s!(M_s - 1)!}, \tag{1.1}$$

available ways that the particles can be distributed. To see how this factor arises, imagine each available quantum state as a box which can hold any number of identical balls, as sketched in Fig. 1.1. We can count the number of arrangements by seeing that the N_s balls and the $M_s - 1$ walls between boxes can be arranged in any order. Basically there are a total of $N_s + M_s - 1$ different objects arranged in a line, N_s of those are of one type (particles) while $M_s - 1$ of them are of another type (walls between boxes). If we had $N_s + M_s - 1$ distinguishable objects, we could arrange them in $(N_s + M_s - 1)!$ ways. But the N_s particles are indistinguishable as are the $M_s - 1$ walls, giving a reduction by a factor $N_s!(M_s - 1)!$, hence giving the total number of configurations in Eq. 1.1.

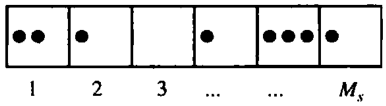

Fig. 1.1 N_s boson particles in M_s available quantum states. We can count the number of possible configurations by considering that the N_s identical particles and the $M_s - 1$ walls between boxes and can be arranged along a line in any order. For bosons each box can hold any number of particles, 0, 1, 2 ....

We now apply this combinatoric rule to the thermodynamics of an ideal gas of N boson particles occupying a volume V. Using periodic boundary conditions, any individual atom will be in a plane-wave quantum state,

$$\psi(\mathbf{r}) = \frac{1}{V^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{1.2}$$

where the allowed wave vectors are

$$\mathbf{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right), \tag{1.3}$$

and where L_x, L_y, and L_z are the the lengths of the volume in each direction. The total volume is $V = L_x L_y L_z$, and therefore an infinitessimal volume $d^3k = dk_x dk_y dk_z$ of k-space contains

$$\frac{V}{(2\pi)^3} d^3k \tag{1.4}$$

quantum states.[3]

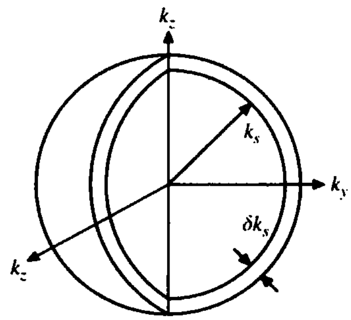

Fig. 1.2 A thin shell of states of wave vector between k_s and $k_s + \delta k_s$. The shell has volume $4\pi k_s^2 \delta k_s$ and so there are $4\pi k_s^2 \delta k_s V/(2\pi)^3$ quantum states in the shell.

[3]The volume *Band Theory and Electronic Properties of Solids*, by John Singleton (2001), in this **Oxford Master Series in Condensed Matter Physics** series explains this point more fully, especially in Appendix B.

Each of these single particle quantum states has energy

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}, \tag{1.5}$$

where m is the particle mass. We can therefore divide up the available single particle quantum states into a number of thin spherical shells of states, as shown in Fig. 1.2. By Eq. 1.4 a shell of radius k_s and thickness δk_s contains

$$M_s = 4\pi k_s^2 \delta k_s \frac{V}{(2\pi)^3} \tag{1.6}$$

single particle states. The number of available states between energy ϵ_s and $\epsilon_s + \delta\epsilon_s$ is therefore

$$\begin{aligned} M_s &= \frac{V m^{3/2} \epsilon^{1/2}}{\sqrt{2}\pi^2 \hbar^3} \delta\epsilon_s, \\ &= V g(\epsilon_s) \delta\epsilon_s, \end{aligned} \tag{1.7}$$

where

$$g(\epsilon) = \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \epsilon^{1/2} \tag{1.8}$$

is the density of states per unit volume, shown in Fig. 1.3.

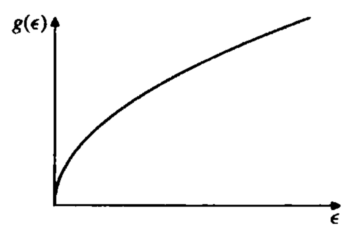

Fig. 1.3 The single particle density of states, $g(\epsilon)$, of a three dimensional gas of particles.

The fundamental principles of statistical mechanics tell us that the total entropy of the gas is $S = k_{\mathrm{B}} \ln W$, where k_{B} is Boltzmann's constant and W is the number of available microstates of a given total energy E. To determine W we must consider how the N atoms in the gas are distributed among the k-space shells of states of different energies. Suppose that there are N_s atoms in shell s. Since there are M_s quantum states in this shell, then we can calculate the total number of available quantum states for this shell using Eq. 1.1. The total number of available microstates for the whole gas is simply the product of the number of available states in each k-space shell,

$$W = \prod_s W_s = \prod_s \frac{(N_s + M_s - 1)!}{N_s!(M_s - 1)!}. \tag{1.9}$$

Using Stirling's approximation, $\ln N! \sim N \ln N - N$, and assuming that N_s, $M_s >> 1$, we have the entropy

$$S = k_{\mathrm{B}} \ln W = k_{\mathrm{B}} \sum_s [(N_s + M_s) \ln (N_s + M_s) - N_s \ln N_s - M_s \ln M_s]. \tag{1.10}$$

In thermal equilibrium the particles will distribute themselves so that the numbers of particles in each energy shell, N_s, are chosen so as to maximize this total entropy. This must be done varying N_s in such a way as to keep constant the total number of particles,

$$N = \sum_s N_s \tag{1.11}$$

and the total internal energy of the gas

$$U = \sum_s \epsilon_s N_s. \tag{1.12}$$

Therefore we must maximize the entropy, S, with the constraints of fixed N and U. Using the method of Lagrange multipliers, this implies that

$$\frac{\partial S}{\partial N_s} - k_{\mathrm{B}}\beta \frac{\partial U}{\partial N_s} + k_{\mathrm{B}}\beta\mu \frac{\partial N}{\partial N_s} = 0, \tag{1.13}$$

where the Lagrange multiplier constants have been defined as $k_{\mathrm{B}}\beta$ and $-k_{\mathrm{B}}\beta\mu$ for reasons which will be clear below. Carrying through the differentiation we find

$$\ln (N_s + M_s) - \ln N_s - \beta\epsilon_s + \beta\mu = 0. \tag{1.14}$$

Rearranging to find N_s we find the result first obtained by Bose and Einstein,

$$N_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} M_s. \tag{1.15}$$

The average number of particles occupying any single quantum state is N_s/M_s, and therefore the average occupation number of any given single particle states of energy $\epsilon_{\mathbf{k}}$ is given by the **Bose–Einstein distribution**

$$f_{\mathrm{BE}}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}. \tag{1.16}$$

In this formula we still have not properly identified the two constants, β and μ, which were introduced simply as Lagrange multipliers. But we can easily find their correct interpretation using the first law of thermodynamics for a gas of N particles,

$$dU = T\,dS - P\,dV + \mu\,dN, \tag{1.17}$$

where T is the temperature, P is the pressure, and μ is the chemical potential. Rearranging gives

$$dS = \frac{1}{T}(dU + P\,dV - \mu\,dN). \tag{1.18}$$

The entropy is given by $S = k_B \ln W$ calculated from Eq. 1.10 with the values of N_s taken from Eq. 1.15. Fortunately the differentiation is made easy using a shortcut from Eq. 1.13. We have

$$\begin{aligned} dS &= \sum_s \frac{\partial S}{\partial N_s}\,dN_s, \\ &= k_B\beta \sum_s \left(\frac{\partial U}{\partial N_s} - \mu\frac{\partial N}{\partial N_s}\right) dN_s \text{ from Eq. 1.13}, \\ &= k_B\beta(dU - \mu\,dN). \end{aligned} \tag{1.19}$$

Comparing with Eq. 1.18, we see that

$$\beta = \frac{1}{k_B T}, \tag{1.20}$$

and the constant μ which we introduced above is indeed just the chemical potential of the gas.

The method we have used above to derive the Bose–Einstein distribution formula makes use of the thermodynamics of a gas of fixed total particle number, N, and fixed total energy U. This is the **microcanonical ensemble**. This ensemble is appropriate for a system, such as a fixed total number of atoms, such as a gas in a magnetic trap. However, often we are interested in systems of an effectively infinite number of atoms. In this case we take the **thermodynamic limit** $V \to \infty$ in which the density of atoms, $n = N/V$, is held constant. In this case it is usually much more convenient to use the **grand canonical ensemble**, in which both the total energy and the particle number are allowed to fluctuate. The system is supposed to be in equilibrium with an external heat bath, maintaining a constant temperature T, and a particle bath, maintaining a constant chemical potential μ. If the N-body quantum states of N particles have energy $E_i^{(N)}$ for $i = 1, 2, \ldots$, then in the grand canonical ensemble each state occurs with probability

$$P^{(N)}(i) = \frac{1}{\mathcal{Z}} \exp\left[-\beta(E_i^{(N)} - \mu N)\right], \tag{1.21}$$

where the grand partition function is defined by

$$\mathcal{Z} = \sum_{N,i} \exp\left[-\beta(E_i^{(N)} - \mu N)\right]. \tag{1.22}$$

All thermodynamic quantities are then calculated from the grand potential

$$\Omega(T, V, \mu) = -k_B T \ln \mathcal{Z} \tag{1.23}$$

using

$$d\Omega = -SdT - PdV - Nd\mu. \tag{1.24}$$

It is quite straightforward to derive the Bose–Einstein distribution using this framework, rather than the microcanonical method used above.[4]

[4]For the derivation of the Bose–Einstein and Fermi–Dirac distribution functions by this method, see standard thermodynamics texts listed under further reading, or Appendix C in the volume *Band Theory and Electronic Properties of Solids* (Singleton 2001).