SUPERCONDUCTIVITY of METALS and CUPRATES

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This book is dedicated to
the Staff and Students of the
Royal Society Mond Laboratory
Cambridge
1933–1973

Contents

Preface

My aims in writing this book are set out in Chapter 1. It grew, at the prompting of Dr Abe Yoffe, out of lectures in superconductivity which I gave to graduate students of the Cavendish Laboratory, and, after its foundation, to students of the Cambridge IRC in Superconductivity. While writing I have been involved in running the annual IRC Winter School, and it will be obvious to any who know the school that I have benefited much from the courses given by my fellow lecturers from the UK superconductivity community over several years. The book has been read in draft by referees in the UK and in the US whose identities I can only guess at, and parts of it have been read in Cambridge by my colleagues Archie Campbell, John Cooper, Gil Lonzarich, John Loram, Andy Mackenzie, David Morgan, Andy Pauza, Brian Pippard and Joe Wheatley; the production at Institute of Physics Publishing has been in the capable hands of Jim Revill, Kathryn Cantley, Peter Binfield, Pamela Whichard and my patient and thorough desk editor Sara Gwynn: all, known and unknown, have made very constructive contributions, and I am grateful. My most important debt is to the teachers, colleagues, students and visitors who, over many years, have been helping me to get my ideas straight. There are too many to cite them all by name, but I must mention especially Brian Pippard, Brian Josephson and David Shoenberg (to whose own book on superconductivity I hope that mine can prove a useful successor).

During the writing, I have frequently been alarmed by the feeling that the subject was moving faster than I was. I can only hope that parts of the book are solid enough to stand the test of a little time.

John Waldram
Cambridge — March 1996

1 Introduction

1.1 The aims of this book

In this book I aim to provide what most research workers entering the field for the first time need to know about superconductivity. Though it is not aimed at professional theoreticians, it contains a good deal of theory, and plunges into theoretical ideas from the second chapter. I make no apology for this: superconductivity is a subtle phenomenon whose proper understanding involves quite deep, though essentially simple, concepts, which experimentalists as well as theoreticians need to be familiar with. In particular, superconductivity is an essentially *quantum-mechanical* phenomenon. I have assumed knowledge of a good undergraduate quantum mechanics course for physicists. I have also assumed a working knowledge of solid-state physics and the thermal physics associated with it.

But the book is not meant only for physicists. Parts of it are intended to be accessible to graduate chemists, engineers and materials scientists (particularly Chapters 3–6, 12–15 and 18), but such readers will probably either have to take much of Chapter 2 on trust or do some homework on the quantum mechanics of charged particles in magnetic fields. I hope that the same chapters will also prove useful in introductory courses intended for undergraduates. Some suggestions for background reading appear after the Appendix at the end of the book.

In the remainder of this chapter we shall review briefly the early history of the subject and explain how the book is laid out.

1.2 The absence of electrical resistance

Superconductivity was discovered at Leiden by Kamerlingh Onnes in 1911 [1], soon after helium had first been liquefied in the same laboratory. What he found was that in pure mercury (and the same effect was soon found in tin, lead and other metals) the electrical resistance disappeared abruptly below a certain critical temperature, T_c, and that, to his surprise, deliberately increasing the scattering by making the mercury impure did not affect the disappearance of resistance. In homogeneous samples the loss of resistance at T_c is remarkably abrupt and complete. One can, for instance, set up a circulating supercurrent in a superconducting lead ring and observe no perceptible fall in the current over several months if the ring is kept below T_c.

We now know that the same phenomenon occurs in about half the metals of the periodic table (Table 1.1). The critical temperatures for the elements are all low, the highest being for niobium, at 9.25 K, which explains why the effect was not observed earlier. Since 1986, however, we have known that in certain complex cuprates the effect occurs at much higher temperatures: Figure 1.1 shows an example.

Table 1.1. Superconducting transition temperatures of the most common forms of the elements, in K. Other elements become superconducting under pressure. None of the rare earths is superconducting at atmospheric pressure.

H																	He
Li	**Be**											B	C	N	O	F	Ne
	0.03																
Na	Mg											**Al**	Si	P	S	Cl	A
												1.18					
K	Ca	Sc	**Ti**	**V**	Cr	Mn	Fe	Co	Ni	Cu	**Zn**	**Ga**	Ge	As	Se	Br	Kr
			0.4	**5.4**							**0.85**	**1.08**					
Rb	Sr	Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	Rh	Pd	Ag	**Cd**	**In**	**Sn**	Sb	Te	I	Xe
			0.81	**9.25**	**0.92**	**7.8**	**0.49**				**0.52**	**3.4**	**3.72**				
Cs	Ba	**La**	**Hf**	**Ta**	**W**	**Re**	**Os**	Ir	Pt	Au	**Hg**	**Tl**	**Pb**	Bi	Po	At	Rn
		6.0	**0.13**	**4.47**	**0.02**	**1.70**	**0.66**				**4.15**	**2.38**	**7.19**				
Fr	Ra	Ac	**Th**	**Pa**	**U**												
			1.38	**1.4**	**0.25**												

If there is no resistance, it seems that the electric field $\boldsymbol{E}$ must be zero in a superconductor. It was quickly discerned that in consequence, according to Faraday's law $\oint \boldsymbol{E} \cdot \mathrm{d}\boldsymbol{l} = -\partial\Phi/\partial t$, the magnetic flux enclosed by any superconducting loop must be constant. Thus rings of superconductor carrying a current should *trap* a fixed amount of flux and, on applying

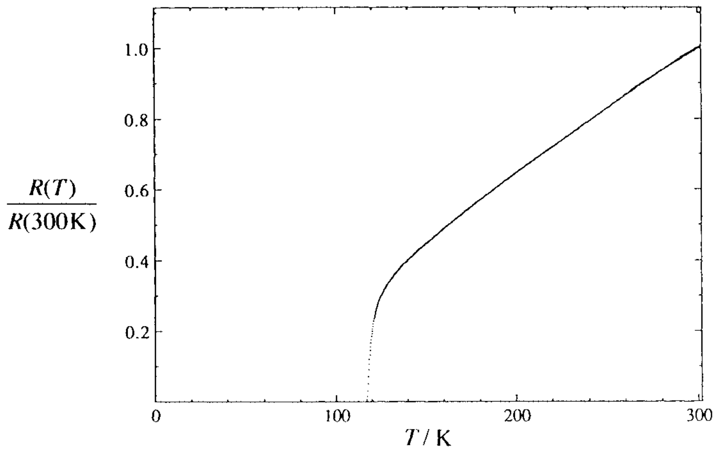

Figure 1.1. Resistivity of a sample of Tl2223 cuprate as a function of temperature (after Loram *et al* [2]).

a magnetic field to a bulk sample, screening currents must flow on the surface which *prevent the field from entering the bulk.* These predictions were confirmed.

If the magnetic field applied to a bulk sample is increased, the screening supercurrents flowing on its surface must also increase. It is not surprising that, as Kamerlingh Onnes discovered in 1913 [3], there is a limit to this process: when a magnetic field is applied parallel to a long straight rod with no demagnetizing coefficient, there is a critical field beyond which the surface supercurrents can no longer exclude flux from the bulk. For the type I superconductors first discovered this was the *thermodynamic critical field* B_c: at this field the supercurrents collapsed completely and the metal entered the normal state. The thermodynamic critical field rises as the temperature falls (Figure 1.2).

Wires of superconductor also have a *critical current* I_c. For simple superconductors this is given by *Silsbee's rule*: the critical current is equal to $2\pi r B_c/\mu_0$ where r is the radius of the wire, the current which generates the critical field at the surface of the wire.

In 1927 Meissner showed [4] that the absence of electric field applied also to thermoelectric effects: there is no *Seebeck voltage* in superconductors, and in fact all the usual thermoelectric effects are absent.

1.3 Thermal properties and the two-fluid model

Measurement of the electronic heat capacity of tin by Keesom and Kok in 1932 [5] showed that in the superconducting state the heat capacity varied

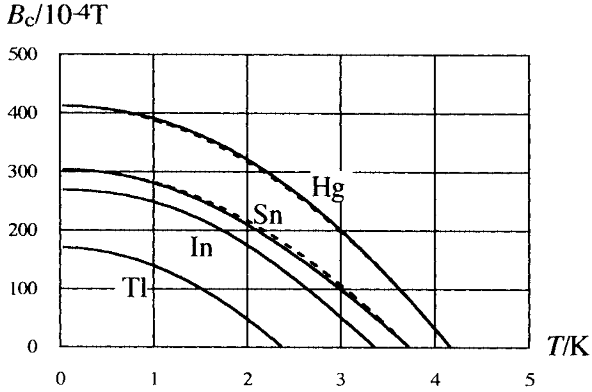

Figure 1.2. Thermodynamic critical fields of some superconducting elements as a function of temperature (solid curves). As a useful approximation we may write $B_c(T) = B_c(0)(1-(T/T_c)^2)$ (broken curves for Sn and Hg). See also Figure 11.10(a).

roughly as T^3, rising above the linear heat capacity of the normal state as T_c was approached, and falling back to the normal value with a vertical discontinuity at T_c, with no latent heat at the transition (Figure 3.2).

The heat capacity anomaly at T_c was of the sort usually associated with a higher-order phase transition involving an *ordering process*, like the appearance of ferromagnetism below the Curie temperature. This and other early results suggested that superconductivity is due to the appearance below T_c of a group of electrons which have *condensed* into a new type of highly ordered quantum state, whose current, for some unknown reason, could not be removed gradually by the usual scattering mechanisms. The absence of thermoelectric effects could be explained if the condensed electrons were so highly ordered as to carry no entropy. (Similar ideas were at that time being discussed to explain the parallel phenomenon of superfluid ^{4}He, which appeared to contain a superfluid component which had no viscosity.)

In 1934 Gorter and Casimir [6] therefore introduced a *two-fluid model* in which the electrons were divided into a *normal fluid*, carrying entropy and subject to scattering, and a *superfluid* condensate, carrying no entropy and subject to no scattering. They did not assume that the electrons in the normal fluid were just like those in a normal metal (nor is this true in newer microscopic theories); on the contrary, they assumed empirically that the free energy of the normal fluid was proportional not to the fraction f_n of normal electrons, but to $\sqrt{f_n}$. This choice was made so as to fit the electronic heat capacity in the superconducting state, then thought to be proportional to T^3. Their theory predicted that $f_n = (T/T_c)^4$, and this later received some confirmation from early work on the magnetic penetration depth in tin (Section 2.5). As we shall see in Chapter 2, the two-fluid model has some basis in the microscopic theory, but the numerical predictions of Gorter and Casimir are best regarded as very approximate fits to the parameters of the true theory, and should only be used with great caution.

The workers in Leiden also measured the thermal conductivity, and showed that in pure superconductors it *fell* rapidly (though not discontinuously) with falling temperature, and eventually at the lowest temperatures reached values similar to those of electrical insulators (see Figures 8.2 and 14.2). In very dirty alloys, however, the thermal conductivity *rose* above the normal-state value as temperature fell. This behaviour was at least qualitatively in accord with the two-fluid model: in the clean material the thermal conduction was normal-electron dominated (the superelectrons carried no entropy), and fell because the number of normal electrons was falling; but in very dirty alloys the conductivity was phonon dominated, and rose because the phonons were being scattered less by the smaller number of normal electrons.

1.4 Type I and type II superconductors

It became understood in the 1950s that superconductors fall into two classes, depending on the sign of the surface energy of a superconducting–normal interface. Almost all of the pure elementary superconductors studied before 1940 proved to be of type I, with a positive interface energy. Type I superconductors show a reversible first-order phase transition with a latent heat when the applied field reaches B_c; and at this particular field relatively thick normal and superconducting domains running parallel to the field can coexist, in what is known as the *intermediate state.*

It had been known since the 1930s that superconducting alloys often contained trapped magnetic flux, showed a large magnetic hysteresis and continued to be superconducting at fields much greater than the thermodynamic critical field B_c predicted from their heat capacities. For many years this was put down to 'dirt effects'—supposed inhomogeneities, with some sort of network of highly superconducting regions threading a matrix with much weaker condensation—but in 1951 a new and important phenomenological theory proposed by Ginzburg and Landau made it possible to calculate the behaviour of superconductors in which the order parameter varied strongly from point to point. It gradually became clear that the alloys were simply *type II superconductors*, with a negative interface energy, and that many of their properties were intrinsic. In such materials finely divided *quantized flux vortices* or *flux lines* entered the material over a range of applied fields below B_c, and remained stable over a range of applied fields extending far above B_c, in what became known as the *mixed* *state*. If these flux lines were *pinned* by lattice defects or other agencies, the type II superconductor could carry a large supercurrent, greatly exceeding the Silsbee's rule criterion, in very high magnetic fields. It was this which made possible the development during the 1960s and 1970s of useful high-field superconducting magnets. (See Chapters 4 and 5.)

1.5 Other superconducting materials

Table 1.1 shows the transition temperatures of the elements and Table 1.2 shows some important parameters for typical superconductors of various types. Work before 1940 was concentrated largely on soft metal superconductors such as tin, lead and their alloys, but it was subsequently realized that the hard transition elements such as niobium and vanadium had high transition temperatures and were easily made type II by alloying, which allowed them to carry high currents in high fields. NbTi wire, for instance, is commonly used to build superconducting coils operating in fields up to about 9 T.

A large number of compounds were found to be superconducting, and during the 1970s it was discovered that transition metal compounds with the A15 structure gave strongly type II materials having particularly high values of T_c, making possible magnets working up to 20 T. Theoretical work had suggested that organic molecules with half-filled electron levels might become superconducting at high temperatures, and this led to a hunt for superconducting organic molecules, which was successful, though no materials with exceptionally high T_c were found. Very recently interest in organic superconductors has been rekindled through the discovery of superconductors obtained by doping the compound C_{60} with alkali metals. (The molecule of C_{60} forms a hollow sphere and crystallizes in a close-packed lattice with the dopants in the interstices between the spheres.)

In the 1980s great interest developed in *heavy-fermion compounds*, such as UPt_3, materials with strong magnetic interactions which lead to a large mass renormalization for the electrons. Some of these materials turned out to be superconducting and are interesting because both the condensation mechanism and the nature of the ground state are probably different from those of the usual superconductors.

Until 1986 it had been widely believed that superconductivity of the usual type could not exist at temperatures above about 30 K. There was therefore great excitement when in that year Bednorz and Müller [7] discovered superconductivity in an La-doped Ba cuprate at 36 K, and the following year Wu *et al* [8] found it in a related O-doped Y–Ba cuprate at 93 K. Since then superconductivity has been found in a large number of similar cuprate materials at temperatures up to 135 K. Since many of these

Table 1.2. Typical superconductors with important parameters. For anisotropic materials the penetration depth λ and the coherence length ξ_0 are quoted for currents flowing in the highest conductivity direction. γ is the Sommerfeld constant (so γT is the electronic heat capacity per unit volume in the normal state). Notes: (1) The BCS coupling parameter NV is a nominal one obtained from T_c and the Debye temperature using the BCS weak-coupling formula (7.30). (2) These ratios have been computed using the tunnelling value for Δ where this is known. (3) These ratios should be 1.0 for an s-wave BCS weakly coupled superconductor. (4) This ratio should be 1.0 for any s-wave BCS superconductor if the gap parameter is independent of energy. (5) Measured at 8.5 kbar.

		T_c (K)	$B_c(0)$ (T)	$\lambda(0)$ (nm)	ξ_0 (nm)	NV (1)	$\frac{\Delta}{1.76kT_c}$ (2, 3)	$\frac{\Delta\sqrt{1.5\mu_0\gamma}}{k\pi B_c(0)}$ (2, 4)	$\frac{\Delta C}{1.43\gamma T_c}$ (3)
Non-transition elements									
Al	A1	1.175	0.010	50	1600	0.18	0.99	0.96	1.12
Sn	tetragonal	3.721	0.030	51	230	0.25	0.99	0.95	1.12
In	A1	3.405	0.028	64	440	0.30	1.01	1.02	
Pb	A1	7.19	0.080	39	83	0.39	1.21	1.05	1.85
Transition elements									
V	A2	5.4	0.125			0.23	0.97	0.95	1.10
Ta	A2	4.47	0.083			0.25	1.04	1.02	1.10
Nb	A2	9.25	0.127	44	40	0.30	1.04	0.99	1.45
A15 compounds									
Nb_3Ge	A15	23.0			3				
Nb_3Sn	A15	18.2			4				
Heavy-fermion compounds									
UBe_{13}		0.9							
UPt_3		0.45			18				
Organic compounds									
$(TMTSF)_2ClO_4$		1.2	0.003	500	140				
$(TMTSF)_2PF_6$		1.1(5)							
Ceramic cuprates									
$(La/Sr)CuO_4$		36	0.9	100	2.5				
$YBa_2Cu_3O_{7-\delta}$		93	1.0	130	1.5	0.66	1.3	1.25	2

materials are superconducting above 77 K, the boiling point of liquid nitrogen, these discoveries were widely expected to lead to a great flowering of applications, and much effort was poured into superconductivity research, which continues today. (See Chapters 12–18.)

1.6 The layout of this book

The first two chapters provide a key to much that follows. In this introductory chapter we have reviewed the early history of the subject and some of the most significant experimental facts. In Chapter 2 we shall introduce the basic idea of the *effective superfluid wavefunction* and show how the celebrated *London equations* which describe the electrodynamics of superconductors may be derived from it. We shall then describe and explain the simplest *macroscopic quantum phenomena* associated with superfluids, such as the Meissner effect, the magnetic skin depth and the quantization of trapped flux. Chapter 2 will make no direct reference to the microscopic theory, but will foreshadow some of the ideas which appear in it.

Chapters 3–6 cover those basic aspects of superconductivity which involve only the thermodynamic and superfluid properties, and can be understood without knowing the microscopic theory. Note that these chapters include two of the most useful theoretical formulations—the Ginzburg–Landau theory of the non-uniform superconductor in a magnetic field and the Josephson picture of supercurrent passing through weak links—both of which can be presented in purely phenomenological terms. They also include two topics dependent on these formulations—the mixed state and the Josephson effects—on which the most important applications of superconductivity depend. The applications themselves are covered in Chapter 18.

Chapters 12–16 cover the basic properties of the high-temperature cuprate superconductors. When this book was planned an enormous amount of work on these materials was under way, and I had expected that their essential physics would be quickly understood. This has not in fact happened, so these chapters remain tentative and at some points speculative. For the same reason I have tried to keep to essentials and to keep them short.

The remaining chapters, Chapters 7–11, 16 and 17, are concerned with the full microscopic theory, which almost everyone finds difficult. My aim in these chapters has been to make the theory more accessible to and usable by experimentalists, rather than to provide a treatise which would satisfy a theoretician. This theory can only usefully be written down using the formalism of *second quantization*, and for readers unfamiliar with it a brief introduction is provided in the Appendix. Chapters 7 and 8 cover the basic Bardeen–Cooper–Schrieffer (BCS) theory, which has been so very successful for conventional superconductors, and Chapters 9–11 extend it in various ways. These chapters also cover those experimental phenomena which are best discussed in the context of microscopic theory, including the transport and high-frequency properties of the superconducting state, tunnelling through barriers, the proximity effect (the spreading of superconductivity into neighbouring normal metals), normal–superconducting (NS) boundary physics and non-equilibrium effects. Chapter 16 compares the cuprates with BCS theory. Chapter 17 provides a brief account of various alternative theories for the cuprate superconductors, on which there is yet no clear consensus.

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2 The superfluid

In this chapter we shall examine the characteristic *superfluid properties* of superconductors, as phenomena. The microscopic theory which underlies these phenomena appears in Chapters 7–11.

2.1 The two-fluid model in BCS theory

The first successful description of superconductors was the *two-fluid model*, developed by Gorter and Casimir in the 1930s [1]. According to the two-fluid model, a superconductor behaves as though it contains electrons of two different types, the *normal electrons*, which behave at least approximately like electrons in normal metals, and the *superelectrons*, which have striking and unusual properties. Both types of electron can carry current: the normal electrons with resistance and the superelectrons without resistance. The normal electrons can carry heat, but the superfluid is supposed to be perfectly ordered, has no entropy and can carry no heat. As we pass below the critical temperature T_c, the density of superfluid is supposed to rise from zero, while the density of normal fluid falls. Since the normal fluid and superfluid conduct in parallel, the d.c. *electrical* conductivity is infinite below T_c, but the *thermal* conductivity falls to zero at $T = 0$.

This simple two-fluid description survives to some extent in the modern microscopic theory first developed by BCS. We shall examine this theory in detail in Chapters 7 and 8, but it may be helpful to give a brief description of some of its features here. The theory is based on the idea that in the superconducting metals there is, surprisingly, a weak *attractive* force acting between electrons near the Fermi level. At temperatures below T_c this force creates a new type of quantum state, somewhat different from the Fermi sea of a normal metal (Figure 2.1). As a rough description, which we shall refine as we proceed, we may say that below T_c the system behaves as though a small proportion of the electrons near the Fermi energy had been bound together in *pairs*, like molecules. The internal motion of the pair is supposed to have no orbital angular momentum (it is an s state), and consequently the two spins must be in a singlet antiparallel spin state to satisfy the requirements of exchange symmetry. However, the pair binding differs in some ways from the ordinary binding of an isolated pair of particles by an attractive force. In conventional superconductors at $T = 0$ the orbital state of the pair has a radius ξ_0 typically of order 10^{-6} m, so large that the individual pairs overlap strongly in space, and the binding turns out to be *cooperative*—the binding energy 2Δ of any one pair depends on how many other pairs have condensed, and, in addition, the external centre of mass motions of all the pairs are coupled together so that each pair is in exactly the same state. (This is possible because a pair of fermions constitutes a *boson*: we sometimes say that the pairs have undergone a *Bose condensation*—many pairs condensed into the same quantum state, like the condensation which occurs for purely statistical reasons in an ideal Bose gas at low temperatures.) As we shall see, it is the presence of the pairs which gives the system its superfluid properties. For instance, if we add two electrons to the superfluid as a bound pair, this has no effect upon the entropy, because the number of ways of arranging the system has not changed: for any number of pairs the pair state is unique. It follows (by minimizing the free energy for the superfluid in contact with an external electron reservoir in which the electrons have electrochemical potential μ) that in thermal equilibrium two electrons entering the superconductor as a bound pair must always enter with energy 2μ. In fact, the superfluid behaves exactly like that otherwise mythical device of statistical thermodynamics the *ideal particle reservoir*, in which all the particles have the same energy μ and no entropy.

The new paired ground state at $T = 0$, as we shall see in more detail later, is not a state with definite occupation of particular k states, but it may be Fourier analysed into such states, and when this is done we find that the average k-state occupation differs only slightly from that in the Fermi sea at $T = 0$: instead of the occupation changing sharply from 1 to 0 at the Fermi surface, the probability of occupation is slightly blurred. (This blurring is a property of the paired ground state itself and has nothing to do with thermal excitation.)

For an ordinary metal the Fermi sea ground state has electron and hole *excitations* which have definite momentum $\hbar \boldsymbol{k}$ and positive excitation energy $\epsilon_{\boldsymbol{k}}$. We create an electron excitation by taking an electron from the imaginary reservoir at energy μ and placing it in a momentum state just outside the Fermi surface, and we create a hole excitation by taking an electron from a momentum state just inside the Fermi surface and placing it in the reservoir. (In superconductivity theory the concept of a 'hole state' refers to an empty state below the Fermi level, and not, as in semiconductor theory, to an empty state at the top of the valence band.) In a

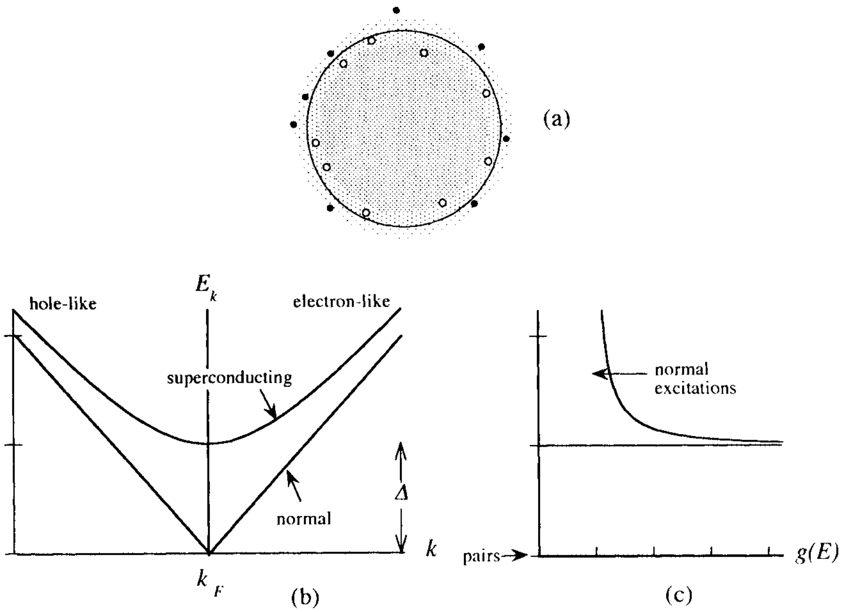

Figure 2.1. BCS theory as it applies to the two-fluid model. (a) The paired BCS ground state is not very different from the Fermi sea, but has a slightly fuzzy Fermi surface. It still has single-particle excitations which are electron-like outside and hole-like inside the Fermi surface. (b) In a superconductor the energy E_k required to bring an excitation of momentum $\hbar \boldsymbol{k}$ from a reservoir of chemical potential μ into the system is not less than Δ. (c) The corresponding density of states for excitations $g(E)$ has a sharp cusp at $E = \Delta$, with an energy gap for $E < \Delta$. But it costs no energy to bring electrons from the reservoir into superfluid pair states.

normal metal the energy needed to create such excitations can be made as small as we like by choosing $\boldsymbol{k}$ near enough to the Fermi surface. It turns out that the paired state, like the Fermi sea, still has excitations which are *electron-like* for momenta just outside the Fermi surface and *hole-like* for momenta just inside. These single-particle excitations are still fermions, with a Fermi distribution in energy at temperature T, and they give the system its normal fluid properties, but they differ from ordinary electron and hole excitations in several respects. For instance, because it takes a finite energy 2Δ to break up one of the condensate pairs when we create two electron-like excitations, the excitation energy $E_{\boldsymbol{k}}$ cannot be less than Δ. The way in which $\epsilon_{\boldsymbol{k}}$ and $E_{\boldsymbol{k}}$ vary with $\boldsymbol{k}$ near the Fermi surface is shown in Figure 2.1(b), and we see that in the superconducting state an *energy gap* for excitations appears at the Fermi level. It follows that in equilibrium the number of normal excitations present will decrease as the temperature is lowered, which is why the effective density of the normal fluid falls to zero at $T = 0$.

Note that we have two different ways of adding electrons to a superconductor. As we have seen, we may add electrons to the superfluid condensate as bound pairs of energy 2μ, without affecting the entropy. We may also add a single electron to the normal fluid by creating an electron-like excitation, corresponding to adding an electron to the normal fluid. Such an electron may enter many different single-particle states with various energies. In general, as in a normal metal, this process will change the number of ways of arranging the system: an electron added to the normal fluid therefore brings entropy with it.

It is important not to imagine that we have two completely independent interpenetrating fluids, because the properties of the single-particle excitations and the pairs interact with each other. For instance, as we have just noted, the energy (and also, as it turns out, the velocity and other properties) of the single-particle excitations depends on the binding energy of the pairs, while the binding energy of the pairs will depend on what single-particle excitations are present. Moreover, as we shall see in the next section, the quantities described as the *normal current* and the *supercurrent* cannot be ascribed in any simple way to the single-particle excitations and the pairs acting alone. There are, however, some situations in which a simple two-fluid description is valid: we shall meet an example in Section 16.6.

2.2 The supercurrent and the superfluid wavefunction

We saw in Section 2.1 that the pairs are energetically coupled together so that each pair is in the same internal orbital state and each pair has the same centre of mass motion. This centre of mass motion may be described by a centre of mass wavefunction $\Psi(\boldsymbol{r})$ which is the same for all the pairs, and is known as the *superfluid wavefunction*. (We shall give a more formal definition later, in Section 9.3.) For instance, a Ψ of the form $\exp(\mathrm{i}\boldsymbol{s}\cdot\boldsymbol{r})$ corresponds to a state in which every pair has the same *momentum* $\hbar\boldsymbol{s}$ (or pair velocity $\boldsymbol{v}_\mathrm{s} = \hbar\boldsymbol{s}/2m_\mathrm{e}$).

Because of the cooperative interaction, the pair momentum is not easily reduced, by elastic scattering for instance. As we have seen, changing the velocity of a *single* pair with respect to all the others would destroy its cooperative binding energy. It is equivalent to breaking up the pair completely, and requires energy of at least 2Δ. At $T = 0$, if the pair velocity is not too big, this energy will be larger than the kinetic energy of the pair, so the process cannot occur (see Section 4.7). At finite temperatures, inelastic processes will be continually breaking up pairs and forming them by recombination, but such processes also cannot change the common pair momentum, because each pair can only condense if it has a momentum

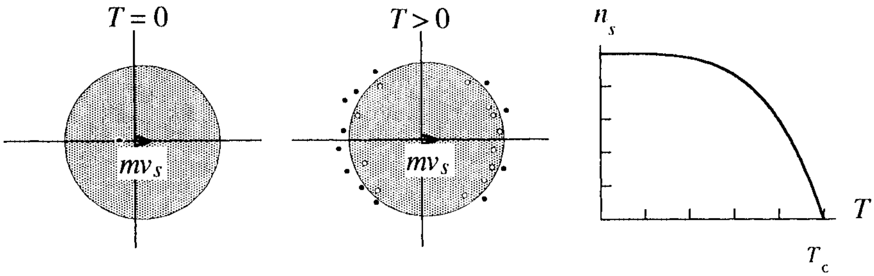

Figure 2.2. The supercurrent for finite v_s. The figures on the left show momentum-space occupations. At $T = 0$ the supercurrent corresponds to giving velocity v_s to *all* the electrons, but for $T > 0$ at the same value of $\boldsymbol{v}_s$ there is a *backflow* in the one-particle excitations, so that J_s and hence the effective density of superelectrons $n_s(T)$ are both reduced.

which matches that of the other pairs already condensed. It will turn out (Section 5.7) that there are some special energetically allowed processes which do change the momenta of all the pairs at once, but they involve flux-line nucleation and are usually exceedingly improbable. Thus the pair momentum has a strong tendency to persist. This suggests that the system may show a *supercurrent*—electric current which flows persistently, without resistance.

We now come to a subtle but important point. The supercurrent is not just the current carried by the relatively small number of bound pairs near the Fermi level acting alone. It is, rather, *the total non-decaying current associated with a given pair momentum.* Suppose, for instance, that we take the paired ground state and set it in motion by giving the same small velocity $\boldsymbol{v}_s$ to every electron (Figure 2.2). This will, of course, automatically give the pairs the same velocity. At $T = 0$ this state is stable: according to the Fermi distribution there will be no single-particle excitations present in equilibrium, because they all have positive excitation energy. Thus, so far as current-carrying ability is concerned, at $T = 0$ the system behaves as though *all* the electrons were superfluid. If we write the supercurrent density as

$$\boldsymbol{J}_s = -n_s e \boldsymbol{v}_s \tag{2.1}$$

then we must identify the effective number density of superelectrons n_s as the total number density of electrons n.

At finite temperatures, however, the situation changes. As we just noted, pairs will be continually breaking up and reforming, but without changing the common pair momentum. How will the single-particle excitations come to equilibrium with the pairs? Keeping the pair momentum fixed means that we keep the fuzzy Fermi surface shifted through a given momentum from its equilibrium position (Figure 2.2). In this situation, the equilibrium Fermi distribution of excitations will have more electrons on the left of the Fermi surface than on the right, because the excitation energies are lower there. Thus the equilibrium distribution of excitations, to which the system decays under the influence of phonon and impurity scattering, has an *excitation backflow* to the left. Unlike the situation in a normal metal, however, this backflow only partly cancels the effect of the original shift, leaving a net current to the right. This residual current is in equilibrium under the influence of scattering and does not decay, and we must therefore regard the whole of it, including the backflow contribution, as supercurrent. However, the backflow contribution increases as T rises. For this reason, the effective density n_s of superelectrons to be used in (2.1) falls as the temperature rises, and reaches zero at T_c.

The picture just described holds so long as the electronic mean free path ℓ is much larger than the size ξ_0 of the bound pairs. Not surprisingly, when the scattering is stronger than this the whole picture of the pair state has to change. It turns out that it is still possible to define Ψ, with the supercurrent related to it in the usual way. But, as we shall see later, in this strong scattering limit the effective density of superelectrons is reduced by a further factor of ℓ/ξ_0 (Section 10.9).

Evidently the effective density of superelectrons n_s which appears in the superfluid transport equation (2.1) has a complicated dependence on T and ℓ which does not correspond at all to the density of the pairs themselves, which is much smaller. This raises the question of how the superfluid wavefunction $\Psi(\boldsymbol{r})$ should be normalized. At first sight it seems natural to make Ψ equal to the actual pair amplitude. It is, however, often more convenient to make $\Psi^*\Psi$ equal to the *effective* density of pairs $n_p = \frac{1}{2}n_s$, and this is the convention usually adopted for the superfluid wavefunction Ψ. With this convention the supercurrent density is $-2e\Psi\Psi^*\boldsymbol{v}_s$, or, more generally,

$$\boldsymbol{J}_s = \frac{\mathrm{i}e\hbar}{2m_e}(\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*). \tag{2.2}$$

This convention is convenient, because it makes the supercurrent have the familiar quantum-mechanical form for a current density, but it is important to remember that the amplitude of Ψ, as here defined, has been fixed in a rather artificial way and is only indirectly related to the actual pair amplitude.

2.3 Introduction of the magnetic vector potential

Magnetic fields and the magnetic vector potential play a large role in the physics of superconductors and we need to be clear about our handling of them. As usual we shall use the *electrostatic potential* $\phi(\boldsymbol{r})$ and the *magnetic vector potential* $\boldsymbol{A}(\boldsymbol{r})$ to describe the electric and magnetic fields

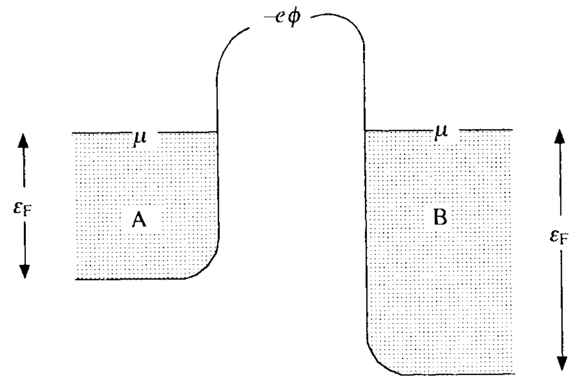

Figure 2.3. Idealized behaviour of the electric potential energy $-e\phi$, the Fermi energy ϵ_F and the electrochemical potential μ at a contact between two metals. Notice that it is μ which is constant in equilibrium.

[2] with

$$\boldsymbol{E} = -\partial \boldsymbol{A}/\partial t - \boldsymbol{\nabla}\phi \tag{2.3}$$

$$\boldsymbol{B} = \boldsymbol{\nabla} \wedge \boldsymbol{A}. \tag{2.4}$$

(These potentials are not uniquely defined, but all the equations of this section are *gauge invariant*—they hold for all possible potential descriptions: see Section 2.7.) In considering electron currents in metals we have to remember the principle of thermodynamics which states that it is the gradient of the *electrochemical potential* μ rather than the gradient of ϕ which determines how the electrons flow: indeed an ordinary voltmeter actually measures differences in μ rather than ϕ [3]. (In a free-electron model we may write $\mu(\boldsymbol{r})$ as $-e\phi(\mathbf{r}) + \epsilon_F(\boldsymbol{r})$—see Figure 2.3.) The driving field for electrons is therefore not the real electric field $\boldsymbol{E}$, but the *effective electric field*, given by

$$\boldsymbol{E}_{\text{eff}} = -\partial \boldsymbol{A}/\partial t + \boldsymbol{\nabla}\mu/e. \tag{2.5}$$

We also need to recall how quantum theory is written in the presence of a magnetic field [4]. For a particle of mass m and charge Q the operator $-i\hbar\boldsymbol{\nabla}$ is the operator for the *canonical momentum* $\boldsymbol{p} = m\boldsymbol{v} + Q\boldsymbol{A}$, and not the usual Newtonian momentum $m\boldsymbol{v}$ [5]. This has some important consequences. For instance, the Schrödinger equation for an electron (with mass m_e, charge $-e$ and canonical momentum $m_e\boldsymbol{v} - e\boldsymbol{A}$) becomes

$$\frac{1}{2m_e}(-i\hbar\boldsymbol{\nabla} + e\boldsymbol{A})^2\Psi - e\phi\Psi = E\Psi. \tag{2.6}$$

(Notice that the first term still represents the Newtonian kinetic energy $\frac{1}{2}m_e v^2$.) Expression (2.2) for the supercurrent density $-2e\Psi\Psi^*\boldsymbol{v}_s$ now takes the form

$$\boldsymbol{J}_{\rm s} = \frac{\mathrm{i}e\hbar}{2m_{\rm e}}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - \frac{2e^2}{m_{\rm e}}\Psi\Psi^*\,\boldsymbol{A}. \tag{2.7}$$

For applications later in this chapter it will be convenient to rewrite this expression in a simpler form. If we write Ψ in terms of its amplitude and phase as $\sqrt{n_{\rm p}}\,\mathrm{e}^{\mathrm{i}\theta}$, (2.7) reduces to

$$\boxed{\Lambda\boldsymbol{J}_{\rm s} = -\left(\frac{\hbar}{2e}\nabla\theta + \boldsymbol{A}\right)} \tag{2.8}$$

where we have introduced the *London parameter* $\Lambda = m_{\rm e}/n_{\rm s}e^2$. Here $\Lambda\boldsymbol{J}_{\rm s}$ is $-m_{\rm e}\boldsymbol{v}_{\rm s}/e$ written in terms of $\boldsymbol{J}_{\rm s}$, and $\hbar\nabla\theta$ is the local canonical pair momentum. We also know that the local pair energy is 2μ. Since the rate of change of phase of the pair wavefunction is related in the usual way to the local pair energy, we have

$$\boxed{\hbar\frac{\partial\theta}{\partial t} = -2\mu.} \tag{2.9}$$

As we shall see shortly, equations (2.8) and (2.9) contain much of the essential physics of the superfluid.

2.4 The first London equation and perfect conductivity

If we take the time derivative of (2.8) we find with the help of (2.9) that

$$\frac{\partial(\Lambda\boldsymbol{J}_{\rm s})}{\partial t} = -\partial\boldsymbol{A}/\partial t + \nabla\mu/e$$

or

$$\boxed{\frac{\partial(\Lambda\boldsymbol{J}_{\rm s})}{\partial t} = \boldsymbol{E}_{\rm eff}} \tag{2.10}$$

where $\boldsymbol{E}_{\rm eff}$ is the effective driving field for electrons in the superconductor introduced in Section 2.3. This result is known as the *first London equation*. (The correct electrodynamic equations for superconductors were first written down by Fritz and Heinz London in a celebrated paper of 1935 [6], and Fritz London shortly afterwards showed their connection with an equation of the form (2.7) [7], though the idea that *pairs* were involved did not emerge until much later.) Equation (2.10) is clearly an *acceleration equation*: it may be rewritten as $\partial\boldsymbol{J}/\partial t = (n_{\rm s}e^2/m)\boldsymbol{E}_{\rm eff}$, which is what one would expect for the free acceleration of superelectrons in an electric field. It implies that after a short pulse of electric field the system will be left with a supercurrent which will not decay, and this, of course, is the property of *superconductivity.*

The above analysis is *not* a proof from first principles of the property of superconductivity. We noted earlier that we can only expect to see superconductivity if the decay of pair momentum by scattering or other processes is inhibited for some reason. The same assumption is built into our derivation. In using equation (2.9) in the presence of a supercurrent we tacitly assumed that the superelectrons remain in thermal equilibrium with the particle reservoir and have energy μ, even when in motion. This assumption is only valid if the superelectrons remain in a unique state which is incapable of decaying. We still have to look to microscopic theory to see why this happens, and shall return to this question in Section 9.4. The first London equation is valuable not as a 'proof' of the property of superconductivity but as a description of how the supercurrent accelerates when an electric field is present.

The property of superconductivity can be exceedingly useful, most obviously, perhaps, in building powerful electromagnets which absorb no power (Section 18.14) and in making microprocessor elements which dissipate no heat (Section 18.8), but it can also be helpful to the low-temperature experimentalist. An ordinary solder-coated copper wire is superconducting at liquid helium temperatures and can be very useful in the leads of a potentiometer measuring tiny voltages of order 10^{-15} V, for instance. As we shall see later, such a wire may be driven normal by quite modest magnetic fields, but wires with superconducting cores having critical fields of 10 T or more are commercially available, from which one can easily wind small magnet coils and flux transformers (Section 18.5).

2.5 The second London equation and perfect diamagnetism

If we take the curl of (2.8) we find, since the curl of a gradient is always zero, that

$$\boxed{\boldsymbol{\nabla} \wedge (\Lambda \boldsymbol{J}_{\mathrm{s}}) = -\boldsymbol{B}.} \tag{2.11}$$

This is the *second London equation.* It is in some respects the analogue for the supercurrent of Ohm's law and shows how a steady supercurrent is a function of the magnetic rather than the electric field.

Using the second London equation, we may show that an applied magnetic field should only penetrate a very short distance into a superconductor. We first write down Ampère's rule as

$$\boldsymbol{\nabla} \wedge \boldsymbol{B} = \mu_0(\boldsymbol{J}_{\mathrm{s}} + \boldsymbol{J}_{\mathrm{res}}) \tag{2.12}$$

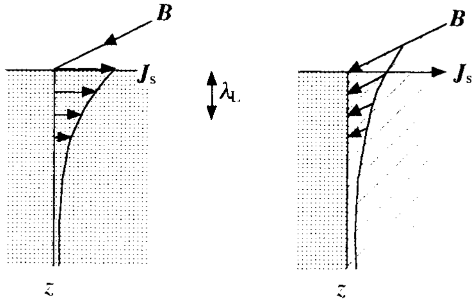

Figure 2.4. The magnetic field $\boldsymbol{B}$ and current density $\boldsymbol{J}_s$ both decay exponentially with distance z into a bulk superconductor, with characteristic decay length λ_L, the *London penetration depth.*

where $\boldsymbol{J}_{res}$ represents any residual current density which may be present in addition to the supercurrent (such as a thermoelectric current in the normal electrons, for instance). Then on taking the curl of (2.12) we find that

$$\nabla \wedge (\nabla \wedge \boldsymbol{B}) = \mu_0 \nabla \wedge (\boldsymbol{J}_s + \boldsymbol{J}_{res})$$

or

$$\nabla^2 \boldsymbol{B} = \frac{\mu_0}{\Lambda} \boldsymbol{B} - \mu_0 \nabla \wedge \boldsymbol{J}_{res} \tag{2.13}$$

assuming that Λ is independent of position, since $\nabla \wedge (\nabla \wedge \boldsymbol{B}) = \nabla(\nabla \cdot \boldsymbol{B}) - \nabla^2 \boldsymbol{B}$ and $\nabla \cdot \boldsymbol{B} = 0$. In almost all practical situations we have either $\boldsymbol{J}_{res} = 0$ or $\nabla \wedge \boldsymbol{J}_{res} = 0$ (for an exception see Section 2.9) and thus

$$\boxed{\nabla^2 \boldsymbol{B} = \frac{\boldsymbol{B}}{\lambda_L^2}} \tag{2.14}$$

where λ_L is the *London penetration depth* $(\Lambda/\mu_0)^{\frac{1}{2}} = (m_e/\mu_0 n_s e^2)^{\frac{1}{2}}$. This result has the form of a *screening equation.* For instance, near a plane surface the magnetic field and the supercurrent density both decay exponentially with depth z as e^{-z/λ_L} (Figure 2.4). The characteristic decay length λ_L is small—of order 10^{-6} m at $T = 0$ in most superconductors, but becoming infinite at T_c where n_s tends to zero. (We shall discuss measurements of the penetration depth later, in Section 10.10.)

It follows from the screening equation that any applied magnetic field should be completely excluded from the bulk of a superconductor by strong screening currents flowing in the very thin skin depth region near the free surface. This is the property of *perfect diamagnetism* and is what is observed for well-annealed samples of type I superconductors such as tin or lead. The property is sometimes described by saying that a bulk type I superconductor is a magnetic material with permeability $\mu = 0$ and susceptibility $\chi_m = -1$. Note that our derivation of this result was based on

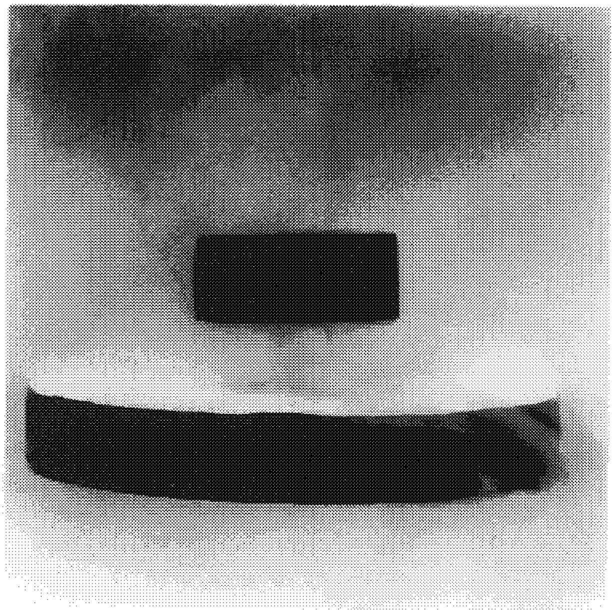

Figure 2.5. A small sample of ceramic superconductor at liquid nitrogen temperature, levitated over a ferromagnet. There is a repulsion between the magnet and the induced screening currents flowing in the superconductor. (Reproduced by permission of the Cavendish Laboratory, University of Cambridge.)

(2.7), and hence on the notion that the supercurrent can be described in terms of the superfluid wavefunction $\Psi(\boldsymbol{r})$. Again it is necessary to appeal to microscopic theory if we wish to understand why this is so.

The property of perfect diamagnetism can be very useful. It may be used, for instance, to levitate small objects, providing an almost completely frictionless suspension (Figure 2.5), and at liquid helium temperatures a simple sheath of superconducting lead foil provides an almost perfect shield against all electric and magnetic fields.

It is important to notice that the two London equations, though closely related, are independent, and neither can be deduced from the other. For instance, if we try to obtain (2.10) by first taking the time derivative of (2.11) and then integrating in space, we cannot fix the term in $\boldsymbol{\nabla}\mu$ on the right-hand side of (2.10) with certainty. Thus, although it is obvious that the screening currents which flow on the surface of a superconductor in a magnetic field must be resistanceless because they do not decay with time, we cannot prove that the effective electric field inside the superconductor is zero using the second London equation alone.

Conversely, it is true that we can get the time derivative of (2.11), but not (2.11) itself, by taking the curl of (2.10). Using the time derivative of Ampère's rule, we can also get the time derivative of (2.14). By integrating with respect to time we may deduce that *changes* in $\boldsymbol{B}$ are screened from the bulk of the superconductor. Equation (2.14), on the other hand, is stronger: it implies that *the field* $\boldsymbol{B}$ *itself* is zero deep inside a superconductor.

However, not all superconductors show this ideal screening behaviour, as we shall now see.

2.6 The Meissner effect, flux trapping and flux quantization

It is interesting to ask whether magnetic flux can ever be *trapped* inside a superconductor. (For a material which simply becomes a perfect conductor in the sense that the carriers have inertia but negligible damping, we expect to find trapped magnetic fields. This is what happens in a plasma, for instance, and it was originally expected that superconductors would behave in the same way.) The screening equation (2.14) suggests that there should be no magnetic flux deep inside a wholly superconducting material—there ought to be no flux trapped in the superconductor itself. It follows that any field originally present should be *expelled* when the material becomes superconducting. This is indeed what happens when carefully annealed samples of type I superconductors are made superconducting by cooling or by reducing the magnetic field below the critical field (Figure 2.6(a)). The effect was first observed by Meissner and Ochsenfeld in 1933 [8] and is usually referred to as the *Meissner effect*. We shall discuss its thermodynamic implications in Section 3.2.

However, we must not conclude too hastily that superconductors cannot trap flux. Suppose we have a piece of type I superconductor in the form of a ring (Figure 2.6(b)). From the first London equation (2.10) we know that the effective electric field $\boldsymbol{E}_{\text{eff}}$ must be zero deep inside the body of the ring, because $\partial \boldsymbol{J}/\partial t = 0$ there. (This applies even if the supercurrents flowing in the ring are changing, because the screening equation (2.14) shows that such currents only flow within the skin depth.) From (2.5) we can deduce that Faraday's law holds in the form

$$\oint \boldsymbol{E}_{\text{eff}} \cdot \mathrm{d}\boldsymbol{l} = -\frac{\mathrm{d}\Phi}{\mathrm{d}t} \tag{2.15}$$

where Φ is the magnetic flux linked with the contour. If the contour is taken around the ring deep inside the material where $\boldsymbol{E}_{\text{eff}} = 0$ we deduce that the flux Φ passing through the ring is conserved. Thus any flux passing through a *ring* of superconductor is indeed trapped: the supercurrents in the ring will adjust themsleves so that the flux passing through the ring

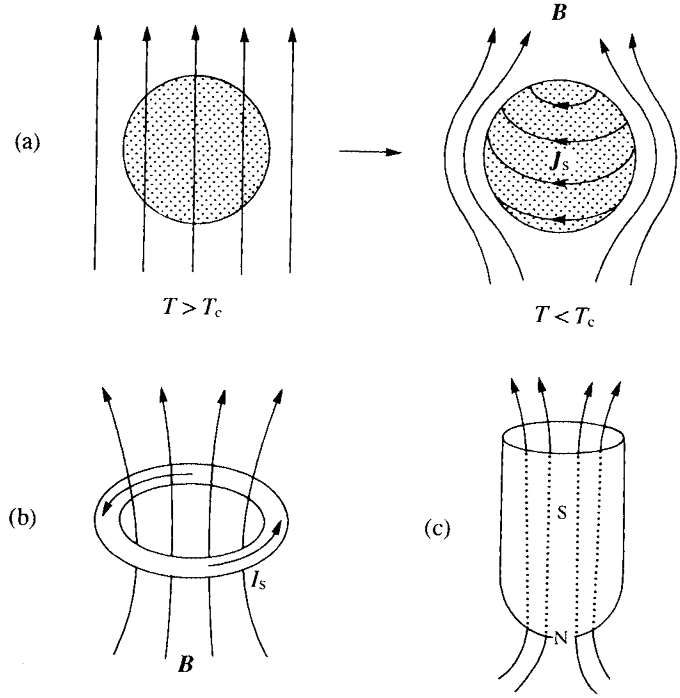

Figure 2.6. Flux expulsion and flux trapping. (a) The *Meissner effect*, the *expulsion* of magnetic flux from a well annealed type I superconductor as it enters the superconducting state, either by cooling or by reducing the field below the critical field. (b) Flux trapped in a ring of superconductor. (c) Flux trapped in a normal region of a superconducting shield either because it was pinned there by defects or because the superconductor was cooled from the outside inwards rather than from the bottom upwards.

never changes. (Experimenters need to remember that at helium temperatures rings of ordinary soft solder, which are common features of metal apparatus, will be superconducting and may trap magnetic flux.)

The same sort of thing may happen with a simply connected piece of superconductor if part of it has been driven normal for some reason. For instance, if a screening lead sheath is cooled from the sides instead of from the bottom, the superconducting region when it first forms may be in the form of a ring and may trap some flux (Figure 2.6(c)). As the superconductor cools, the flux may be compressed into a small region at the bottom of the sheath, where it may provide a field large enough to hold a small region of the sheath normal. If this happens, the sheath will continue to trap flux instead of shielding it. Indeed, behaviour of this sort is common in practice and difficult to avoid.

Even more complex phenomena occur in *type II superconductors.* As we shall see in Chapters 4 and 5, these are materials which may be threaded by *flux lines,* fine threads of flux along which the superconductor has an effectively normal core. In type II superconductors particularly, flux is likely to be pinned inside the material and unable to flow to the surface.

When flux is trapped by a superconductor it is frequently, and interestingly, not only conserved but also *quantized.* Consider what happens if we take the line integral of equation (2.8) around some loop which lies wholly inside a superconductor (Figure 2.7). The line integral of $-\boldsymbol{\nabla}\theta = (2e/\hbar)(\boldsymbol{A} + \Lambda \boldsymbol{J}_\mathrm{s})$ is simply the total decrease in θ as we move once around the loop, and this must be a multiple of 2π since the phase at the starting point must be well defined. Thus

$$\oint (\boldsymbol{A} + \Lambda \boldsymbol{J}_\mathrm{s}) \cdot \mathrm{d}\boldsymbol{l} = \frac{\hbar}{2e} 2\pi n \tag{2.16}$$

where n is an integer. When we are dealing with bulk superconductors and the path of integration lies deep inside the superconductor where $\boldsymbol{J}_\mathrm{s} = 0$, the left-hand side of (2.16) reduces to $\oint \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{l}$, which is just the flux Φ passing upwards through the loop. It follows that this flux is quantized as

$$\Phi = n\Phi_0 \tag{2.17}$$

where n is an integer and Φ_0 is the *flux quantum* defined as

$$\boxed{\Phi_0 = \frac{h}{2e}.} \tag{2.18}$$

(Note the factor of two in the definition of the flux quantum, which arises because we are dealing with a wavefunction for pairs. Φ_0 has the value 2×10^{-15} Wb.) If the superconductor is simply connected and contains no singularities in Ψ then we see by shrinking the loop to a point that we must have $n = 0$, but if the superconductor is in the form of a ring, or if it contains normal regions or flux line singularities (Section 4.10), then n may be non-zero.

Notice, however, that the quantization argument holds only if we can find a loop on which $\boldsymbol{J}_\mathrm{s} = 0$. Cases where this is not possible include rings thin compared to the penetration depth, rings in which there is thermocouple action (Section 2.8) and rotating rings (Section 2.9). In all of these cases the quantized quantity is the left-hand side of (2.16), which is known as the *fluxoid,* and the flux itself is not quantized. The flux is also not quantized for rings containing Josephson junctions (Section 6.5), for a similar reason: we cannot write $-\boldsymbol{\nabla}\theta = (2e/\hbar)\boldsymbol{A}$ in the neighbourhood of the junction.

The quantization of flux in a ring was first detected by Deaver and Fairbank [9] and also by Doll and Näbauer [10], both in 1961. They used a

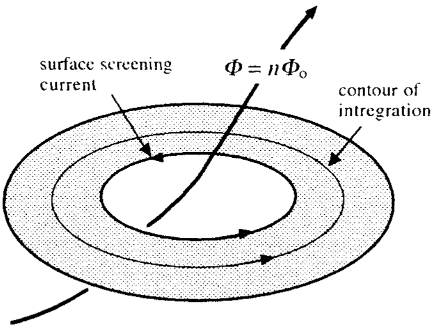

Figure 2.7. Quantization of flux in a multiply connected ring of superconductor.

cylinder of superconducting film evaporated onto a thin fibre. The fibre was cooled in a small parallel magnetic field, which was subsequently removed. The release of flux on warming by the fibre was measured ballistically. More recently, the experimental confirmation by Gough *et al* [11] that the flux quantum in high-T_c superconductors has the same magnitude $h/2e$ shows that, whatever the detailed microscopic theory is in this case, it must still involve a pair wavefunction in some sense. Their experiment was done using a SQUID magnetometer (see Chapter 18) to measure the flux trapped by a ring of sintered material a few millimetres across.

2.7 Gauge transformations and the London gauge

We come now to a rather technical point, but one which proves to be particularly significant for superconductors. In considering the description of the electric and magnetic fields set out in Section 2.3, it is helpful to remember that though the potentials and the wavefunction *describe* physical variables, they are not themselves observable. In fact if we simultaneously transform $\boldsymbol{A}$, ϕ, μ and Ψ as follows

$$\boldsymbol{A} \to \boldsymbol{A} + \boldsymbol{\nabla}\chi \tag{2.19}$$

$$\phi \to \phi - \partial\chi/\partial t \tag{2.20}$$

$$\mu \to \mu + e\partial\chi/\partial t \tag{2.21}$$

$$\theta \to \theta - \frac{2e}{\hbar}\chi \tag{2.22}$$

where θ is the phase of Ψ and $\chi(\boldsymbol{r}, t)$ is an arbitrary differentiable and single-valued function of space and time, we find that the transformation is *purely formal* and has no effect on any observable quantities. For instance, it is easy to see that it has no effect on the fields $\boldsymbol{E}$, $\boldsymbol{E}_{\text{eff}}$ and $\boldsymbol{B}$, or on the value of $\boldsymbol{J}_s$. Such a transformation is called a *gauge transformation.* Observables which do not change under a gauge transformation are said to be *gauge invariant.* Unobservable quantities such as $\boldsymbol{A}, \phi, \mu$ and θ which change in a defined way under a gauge transformation are said to be *gauge covariant.*

Up to this point we have been careful to keep all the equations in this book gauge invariant—they hold in all gauges—but sometimes it is convenient to work in a particular gauge. For instance, if the superconducting wavefunction is single valued (which will be true so long as the superconductor is simply connected and contains no internal flux) it is convenient to choose $\chi(\boldsymbol{r}, t)$ so that θ always remains zero everywhere. This might be called the *rigid gauge*, because the superfluid wavefunction becomes rigid in the sense that the phase of Ψ never changes and the canonical momentum $\boldsymbol{p} = \hbar\nabla\theta$ remains zero when we switch on an applied magnetic field or introduce transport supercurrent. This choice is natural and convenient because it follows from (2.9) that we have indirectly defined μ to be zero everywhere, which means that we may think of all the superelectrons as being in equilibrium with a notional particle reservoir whose energy we have chosen as our zero of energy. Using (2.8) we find that in the rigid gauge the second London equation may be written in the form

$$\Lambda \boldsymbol{J}_s = -\boldsymbol{A}. \tag{2.23}$$

This is equivalent to writing $m_e \boldsymbol{v}_s$ as $e\boldsymbol{A}$: in the rigid gauge the Newtonian momentum of the electrons is represented by the vector potential term *alone.*

We very frequently also know that $\nabla \cdot \boldsymbol{J}_s = 0$. (This will be true so long as normal current is not being converted into supercurrent, as it may be, for instance, at an NS interface or when we have position-dependent thermoelectric normal currents.) It then follows from (2.23) that

$$\nabla \cdot \boldsymbol{A} = 0 \qquad \text{and} \qquad A_n = \Lambda J_{sn}. \tag{2.24}$$

where the second relation is a boundary condition: A_n is the component of $\boldsymbol{A}$ normal to the boundary and J_{sn} is the supercurrent density normal to the boundary, if any. A vector potential which satisfies these conditions is said to be in the *London gauge.* When combined with the requirement $\nabla \wedge \boldsymbol{A} = \boldsymbol{B}$ these conditions of the London gauge fix the value of $\boldsymbol{A}$ for a given field inside the superconductor unambiguously. Moreover, in the London gauge it is easy to show that $\boldsymbol{A}$ obeys the equation $\nabla^2 \boldsymbol{A} = 0$ outside the superconductor and the screening equation $\nabla^2 \boldsymbol{A} = \boldsymbol{A}/\lambda^2$ inside the superconductor. By solving these two equations, subject to the London conditions and appropriate boundary conditions at infinity, one can compute the pattern of fields and supercurrents for superconductors subject to given applied fields or transport currents.

We cannot always use the London gauge in this way, however. In multiply connected superconductors or in type II materials containing flux lines, the phase is not single valued, so we cannot find a gauge transformation which makes the phase the same everywhere, and when normal current is being converted into supercurrent the London gauge no longer corresponds to the rigid gauge.

It is instructive to use the London gauge to discuss the relation between perfect diamagnetism in superconductors and the well-known diamagnetism of atoms. When an atom is placed in a uniform magnetic field $\boldsymbol{B}$, it is well known that the electron assembly undergoes *Larmor precession* with angular velocity $e\boldsymbol{B}/2m_{\mathrm{e}}$, and the corresponding rotation of the assembly gives the atom a diamagnetic moment. In quantum theory we account for this as follows. The uniform field applied to the atom may be described using a vector potential of the form $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \wedge \boldsymbol{r}$, which is in the London gauge. In a weak field, this perturbation has a negligible effect on the wavefunction; as in the superconductor we may say that the wavefunction is *rigid* in this gauge. The formal angular momentum quantum numbers are not changed and the local canonical momentum $\boldsymbol{p}$ is not altered. However, the *interpretation* of the wavefunction does change. Because $\boldsymbol{p} = m_{\mathrm{e}}\boldsymbol{v} - e\boldsymbol{A}$, the electrons now all have an extra local velocity $e\boldsymbol{A}/m_{\mathrm{e}}$, as in the superconductor. In the atom this velocity has the form $(e\boldsymbol{B}/2m_{\mathrm{e}}) \wedge \boldsymbol{r}$, the expected precession velocity. The only important difference in the case of an object as small as an atom is that the diamagnetic current is too weak to screen the applied magnetic field appreciably, whereas in the superconductor, as we have seen, it is strong enough to restrict the field to the region within a penetration depth λ_{L} of the surface.

2.8 Thermoelectric effects

When a temperature gradient exists in a normal metal, processes such as electron–phonon collisions drive the electrons along the temperature gradient: the metal behaves as though it contained a driving electromotive force (EMF), the thermal *Seebeck* EMF. In an isolated sample the electrons flow until a gradient of electrochemical potential is set up which cancels out the effect of the EMF, and dynamic equilibrium is established (Figure 2.8(a)). If two different metals are connected in a loop, the Seebeck EMF corresponding to a given temperature difference may not be the same in each, so in general there will be a net EMF acting in the loop and a thermoelectric current will circulate (Figure 2.8(c)).

In a superconductor something different happens. We cannot set up a gradient of μ, and the thermoelectric forces therefore drive a continuous normal thermocurrent along the sample. We may use the analysis of Section 2.5 in this situation, identifying $\boldsymbol{J}_{\mathrm{res}}$ as the normal thermoelectric