34
Superconductivity

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In Chapter 32 we found that the independent electron approximation cannot adequately describe most magnetically ordered solids. In many metals without any magnetic ordering a still more spectacular failure of the independent electron approximation sets in abruptly at very low temperatures, where another kind of electronically ordered state is established, known as the superconducting state. Superconductivity is not peculiar to a few metals. More than 20 metallic elements can become superconductors (Table 34.1). Even certain semiconductors can be made superconducting under suitable conditions,[1] and the list of alloys whose superconducting properties have been measured stretches into the thousands.[2]

Table 34.1
SUPERCONDUCTING ELEMENTS[a]

H																	He
Li	Be •											B	C	N	O	F	Ne
Na	Mg											Al	Si •	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge •	As	Se •	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb •	Te •	I	Xe
Cs •	Ba •	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi •	Po	At	Rn
Fr	Ra																

La	Ce •	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu								

[a]Elements that are superconducting only under special conditions are indicated separately. Note the incompatibility of superconducting and magnetic order. After G. Gladstone, et al. Parks *op. cit*, note 6.

Legend:

- Al — Superconducting
- Si • — Superconducting under high pressure or in thin films
- Li — Metallic but not yet found to be superconducting
- B — Nonmetallic elements
- Fe — Elements with magnetic order

The characteristic properties of metals in the superconducting state appear highly anomalous when regarded from the point of view of the independent electron approximation. The most striking features of a superconductor are:

[1] Such as application of high pressure, or preparation of the specimen in very thin films. A striking example of the unexpected ways in which superconductivity can be enhanced is provided by bismuth: Amorphous bismuth is a superconductor at *higher* temperatures than crystalline bismuth, which makes no sense at all in the independent electron approximation.

[2] See B. W. Roberts, *Progr. Cryog.* 4, 161 (1964).

1. A superconductor can behave as if it had no measurable DC electrical resistivity. Currents have been established in superconductors which, in the absence of any driving field, have nevertheless shown no discernible decay for as long as people have had the patience to watch.[3]
2. A superconductor can behave as a perfect diamagnet. A sample in thermal equilibrium in an applied magnetic field, provided the field is not too strong, carries electrical surface currents. These currents give rise to an additional magnetic field that precisely cancels the applied magnetic field in the interior of the superconductor.
3. A superconductor usually behaves as if there were a gap in energy of width 2Δ centered about the Fermi energy, in the set of allowed one-electron levels.[4] Thus an electron of energy $\mathcal{E}$ can be accommodated by (or extracted from) a superconductor[5] only if $\mathcal{E} - \mathcal{E}_F$ (or $\mathcal{E}_F - \mathcal{E}$) exceeds Δ. The energy gap Δ increases in size as the temperature drops, leveling off to a maximum value $\Delta(0)$ at very low temperatures.

The theory of superconductivity is quite extensive and highly specialized. Like the theories we have described elsewhere in this book, it is based on the nonrelativistic quantum mechanics of electrons and ions, but beyond that its similarity to the other models and theories we have examined diminishes rapidly. The microscopic theory of superconductivity cannot be described in the language of the independent electron approximation. Even comparatively elementary microscopic calculations for superconductors rely on formal techniques (field theoretic methods) which, while conceptually no more sophisticated than the ordinary methods of quantum mechanics, require considerable experience and practice before they can be used with confidence and understanding.

Consequently, to a greater degree than in other chapters we shall limit our survey of the theory of superconductivity to qualitative descriptions of some of the major concepts, together with statements of a few of the simpler predictions. The reader who wishes to acquire even an elementary working knowledge of the subject must consult one of the many available books.[6]

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[3] The record appears to be $2\frac{1}{2}$ years; S. C. Collins, quoted in E. A. Lynton, *Superconductivity*, Wiley, New York, 1969.

[4] Under a variety of special conditions superconductivity can also occur without an energy gap. Gapless superconductivity can be produced, for example, by introducing a suitable concentration of magnetic impurities. A review is given by K. Maki in *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969. In the context of superconductivity, the term "energy gap" always refers to the quantity Δ.

[5] This is most directly observed in electron tunneling experiments, which are described below along with other manifestations of the energy gap.

[6] Two fundamental references on the phenomenological theory are F. London, *Superfluids*, vol. 1, Wiley, New York, 1954, and Dover, New York, 1954, and D. Shoenberg, *Superconductivity*, Cambridge, 1962. A very brief survey is given by E. A. Lynton, *Superconductivity*, Methuen, London, 1969. The microscopic theory is expounded in J. R. Schrieffer, *Superconductivity*, W. A. Benjamin, New York, 1964, and in the final chapter of A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, Englewood Cliffs, N.J., 1963. A detailed survey of the theoretical aspects of the subject has been given by G. Rickayzen, *Theory of Superconductivity*, Interscience, New York, 1965, and in somewhat less detail by P. de Gennes, *Superconductivity of Metals and Alloys*, W. A. Benjamin, Menlo Park, Calif., 1966. A survey of all aspects of the subject, theoretical and experimental, by many of the leading experts in the field is *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969.

This chapter is organized as follows:

1. A survey of the basic empirical facts about superconductivity.
2. A description of the phenomenological London equation and its relation to perfect diamagnetism.
3. A qualitative description of the microscopic theory of Bardeen, Cooper, and Schrieffer.
4. A summary of some of the fundamental equilibrium predictions of the microscopic theory and how they compare with experiment.
5. A qualitative discussion of the relationship between the microscopic theory, the concept of an "order parameter," and the transport properties of superconductors.
6. A description of the remarkable tunneling phenomena between superconductors predicted by B. D. Josephson.

CRITICAL TEMPERATURE

The transition to the superconducting state is a sharp one in bulk specimens. Above a critical temperature[7] T_c the properties of the metal are completely normal; below T_c superconducting properties are displayed, the most dramatic of which is the absence of any measurable DC electrical resistance. Measured critical temperatures range from a few millidegrees Kelvin[8] up to a little over 20 K. The corresponding thermal energy $k_B T_c$ varies from about 10^{-7} eV up to a few thousandths of an electron volt. This is quite minute compared with the energies we have become accustomed to regarding as significant in solids.[9] Transition temperatures of the superconducting elements are listed in Table 34.2.

PERSISTENT CURRENTS

Figure 34.1 displays the resistivity of a superconducting metal vs. temperature as the critical temperature T_c is crossed. Above T_c the resistivity has the form characteristic of a normal metal, $\rho(T) = \rho_0 + BT^5$, the constant term arising from impurity[10] and defect scattering, and the term in T^5 arising from phonon scattering. Below T_c these mechanisms lose the power to degrade an electric current and the resistivity drops abruptly to zero. Currents can flow in a superconductor with no discernible dissipation of energy.[11] There are, however, some limitations:

1. Superconductivity is destroyed by application of a sufficiently large magnetic field (see below).

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[7] The critical temperature is that at which the transition occurs in the absence of an applied magnetic field. When a magnetic field is present (see below) the transition occurs at a lower temperature, and the nature of the transition changes from second order to first order; i.e., there is a latent heat in nonzero field.

[8] The lowest temperatures at which superconductivity has been sought, to date.

[9] Thus $\mathcal{E}_F \sim 10$ eV, $\hbar\omega_D \sim 0.1$ eV.

[10] We assume there are no magnetic impurities present; see page 687.

[11] When Ampère first proposed that magnetism could be understood in terms of electric currents flowing in individual molecules, it was objected that no currents were known to flow without dissipation. Ampère persisted in his view and was vindicated by the quantum theory, which permits stationary molecular states in which a net current flows (see Chapter 31). A solid in the superconducting state is behaving like one enormous molecule. The presence of an electric current without dissipation in a superconductor is a dramatic macroscopic manifestation of quantum mechanics.

Table 34.2
VALUES OF T_c AND H_c FOR THE SUPERCONDUCTING ELEMENTS[a]

ELEMENT		T_c (K)	H_c (GAUSS)[b]
Al		1.196	99
Cd		0.56	30
Ga		1.091	51
Hf		0.09	—
Hg	α (rhomb)	4.15	411
	β	3.95	339
In		3.40	293
Ir		0.14	19
La	α (hcp)	4.9	798
	β (fcc)	6.06	1096
Mo		0.92	98
Nb		9.26	1980
Os		0.655	65
Pa		1.4	—
Pb		7.19	803
Re		1.698	198
Ru		0.49	66
Sn		3.72	305
Ta		4.48	830
Tc		7.77	1410
Th		1.368	162
Ti		0.39	100
Tl		2.39	171
U	α	0.68	—
	γ	1.80	—
V		5.30	1020
W		0.012	1
Zn		0.875	53
Zr		0.65	47

[a] For type II superconductors, the zero-temperature critical field quoted is obtained from an equal-area construction: The low-field ($H < H_{c1}$) magnetization is extrapolated linearly to a field H_c chosen to give an enclosed area equal to the area under the actual magnetization curve.
[b] At $T = 0$ (K).

Sources: B. W. Roberts, *Progr. Cryog.* **4**, 161 (1964); G. Gladstone, M. A. Jensen, and J. R. Schrieffer, *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969; *Handbook of Chemistry and Physics*, 55th ed., Chemical Rubber Publishing Co., Cleveland, 1974–1975.

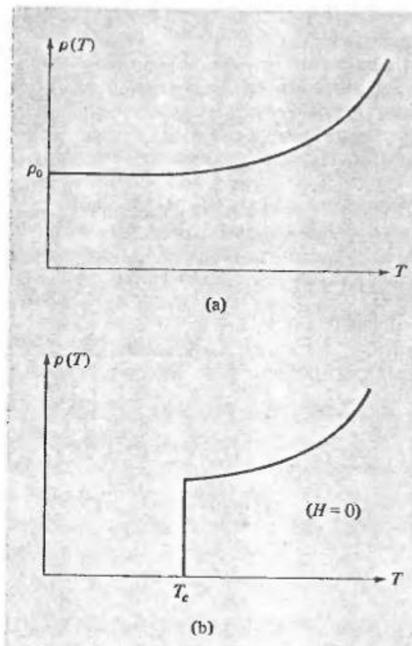

Figure 34.1
(a) Low-temperature resistivity of a normal metal ($\rho(T) = \rho_0 + BT^5$) containing nonmagnetic impurities (b) Low-temperature resistivity of a superconductor (in zero magnetic field) containing nonmagnetic impurities. At T_c, ρ drops abruptly to zero.

2. If the current exceeds a "critical current," the superconducting state will be destroyed (Silsbee effect). The size of the critical current (which can be as large as 100 amp in a 1-mm wire) depends on the nature and geometry of the specimen, and is related to whether the magnetic field produced by the current exceeds the critical field at the surface of the superconductor.[12]
3. A superconductor well below its transition temperature will also respond without dissipation to an AC electric field provided that the frequency is not too large. The change from dissipationless to normal response occurs at a frequency ω of order $\Delta/\hbar$, where Δ is the energy gap.

THERMOELECTRIC PROPERTIES

In the independent electron approximation good electrical conductors are also good conductors of heat, since the conduction electrons transport entropy as well as electric charge.[13] Superconductors, contrary to this, are poor thermal conductors (Figure 34.2).[14] They also exhibit no Peltier effect; i.e., an electric current at uniform temperature in a superconductor is not accompanied by a thermal current, as it would be in a normal metal. The absence of a Peltier effect indicates that those electrons that participate in the persistent current carry no entropy. The poor thermal

[12] See Problem 3.
[13] See page 253.
[14] This property is exploited to make thermal switches.

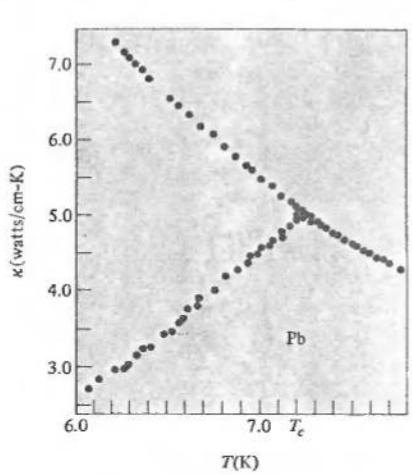

Figure 34.2
The thermal conductivity of lead. Below T_c the lower curve gives the thermal conductivity in the superconducting state, and the upper curve, in the normal state. The normal sample is produced below T_c by application of a magnetic field, which is assumed otherwise to have no appreciable affect on the thermal conductivity. (Reproduced by permission of the National Research Council of Canada from J. H. P. Watson and G. M. Graham, *Can. J. Phys.* **41**, 1738 (1963).)

conductivity indicates that even when a superconductor is not carrying an electric current, only a fraction of its conduction electrons are capable of transporting entropy.[15]

MAGNETIC PROPERTIES: PERFECT DIAMAGNETISM

A magnetic field (provided that it is not too strong) cannot penetrate into the interior of a superconductor. This is most dramatically illustrated by the Meissner-Ochsenfeld effect: If a normal metal in a magnetic field[16] is cooled below its superconducting transition temperature, the magnetic flux is abruptly expelled. Thus the transition, when it occurs in a magnetic field, is accompanied by the appearance of whatever surface currents are required to cancel the magnetic field in the interior of the specimen.

Note that this is not implied by perfect conductivity (i.e., $\sigma = \infty$) alone, even though perfect conductivity does imply a somewhat related property: If a perfect conductor, initially in zero magnetic field, is moved into a region of nonzero field (or if a field is turned on), then Faraday's law of induction gives rise to eddy currents that cancel the magnetic field in the interior. If, however, a magnetic field were established in a perfect conductor, its expulsion would be equally resisted. Eddy currents would be induced to maintain the field if the sample were moved into a field-free region (or if the applied field were turned off). Thus perfect conductivity implies a time-independent magnetic field in the interior, but is noncommittal as to the value that field must have. In a superconductor, the field is not only independent of time, but also zero.

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[15] Presumably the efficacy of the phonons in conducting heat remains undiminished, but this is generally a less important contribution to the thermal conductivity than that of the conduction electrons.

[16] A normal metal is only weakly paramagnetic or diamagnetic (no magnetically ordered metals are superconductors) and an applied magnetic field can penetrate it.

We shall examine the relation between perfect conductivity and the Meissner effect somewhat more quantitatively in our discussion of the London equation below.

MAGNETIC PROPERTIES: THE CRITICAL FIELD

Consider a superconductor at a temperature T below its critical temperature T_c. As a magnetic field H is turned on, a certain amount of energy is expended to establish the magnetic field of the screening currents that cancels the field in the interior of the superconductor. If the applied field is large enough it will become energetically advantageous for the specimen to revert back to the normal state, allowing the field to penetrate. For although the normal state has a higher free energy than the superconducting state below T_c in zero field, at high enough fields this increase in free energy will be more than offset by the lowering of magnetic field energy that occurs when the screening currents disappear and the field is allowed to enter the specimen.

The manner in which penetration occurs with increasing field strength depends in general on the geometry of the specimen. However, for the simplest geometry—long, thin, cylindrically shaped samples with their axes parallel to the applied magnetic field—there are two clearly distinguishable kinds of behavior:

Type I Below a *critical field* $H_c(T)$ that increases as T falls below T_c, there is no penetration of flux; when the applied field exceeds $H_c(T)$ the entire specimen reverts to the normal state and the field penetrates perfectly.[17] The resulting phase diagram in the H-T plane is pictured in Figure 34.3.[18] One often describes this type of field penetration by plotting the macroscopic diamagnetic magnetization density M vs. the applied field H (Figure 34.4a).

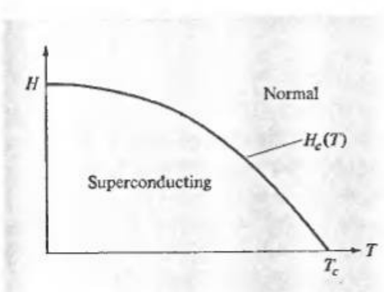

Figure 34.3
The phase boundary between the superconducting and normal states of a type I superconductor in the H-T plane. The boundary is given by the curve $H_c(T)$.

Type II Below a *lower critical field* $H_{c1}(T)$ there is no penetration of flux; when the applied field exceeds an *upper critical field* $H_{c2}(T) > H_{c1}(T)$, the entire specimen reverts to the normal state and the field penetrates perfectly. When the applied field strength is between $H_{c1}(T)$ and $H_{c2}(T)$, there is partial penetration of flux, and the

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17 Except for the small diamagnetic and paramagnetic effects characteristic of normal metals.

18 Some quantitative thermodynamic consequences of this behavior are explored in Problem 1.

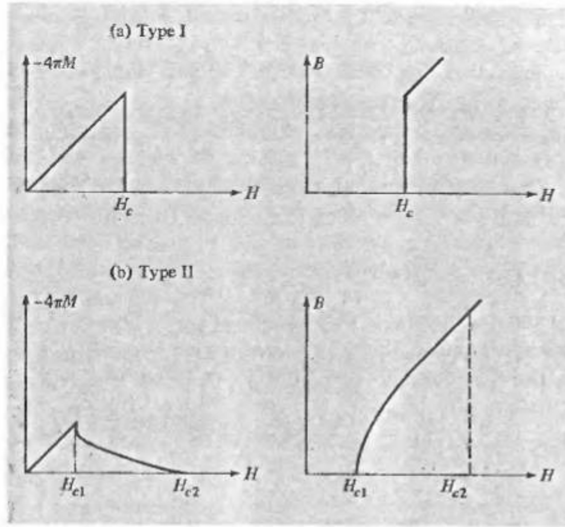

Figure 34.4
(a) Magnetization curve of a type I superconductor. Below H_c no field penetrates: $B = 0$ (or $M = -H/4\pi$). (See footnote 30 for the distinction between B and H in a superconductor.) (b) Magnetization curve of a type II superconductor. Below H_{c1} behavior is as in the type I case. Between H_{c1} and H_{c2}, M falls smoothly to zero, and B rises smoothly to H.

sample develops a rather complicated microscopic structure of both normal and superconducting regions, known as the *mixed state.*[19] The magnetization curve corresponding to type II behavior is shown in Figure 34.4b.

It was proposed by A. A. Abrikosov, and subsequently confirmed by experiment (Figure 34.5), that in the mixed state the field partially penetrates the sample in the form of thin filaments of flux. Within each filament the field is high, and the material is not superconducting. Outside of the core of the filaments, the material remains

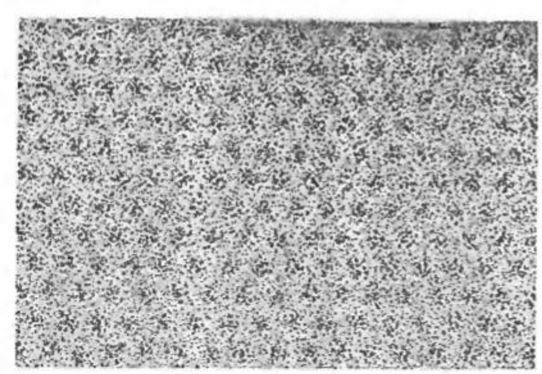

Figure 34.5
Triangular array of vortex lines emerging through the surface of a $Pb_{.98}In_{.02}$ superconducting foil in a field of 80 gauss normal to the surface. (Courtesy of J. Silcox and G. Dolan.) The vortices are revealed by the coagulation of fine ferromagnetic particles. Neighboring vortices are about half a micron apart.

[19] Not to be confused with the *intermediate state*, a configuration a type I superconductor may assume when its shape is more complex than a cylinder parallel to the field, in which macroscopic superconducting and normal regions are interleaved in such a way as to lower the magnetic field energy by more than the cost in free energy of the normal regions.

superconducting, and the field decays in a manner determined by the London equation (see below). Circulating around each filament is a vortex of screening current.[20]

Typical critical fields in type I superconductors are about 10^2 gauss well below the transition temperature. However, in so-called "hard" type II superconductors the upper critical field can be as high as 10^5 gauss, which makes type II materials of considerable practical importance in the design of high-field magnets.

Low temperature critical fields for the elemental superconductors are given in Table 34.2.

SPECIFIC HEAT

At low temperatures the specific heat of a normal metal has the form $AT + BT^3$, where the linear term is due to electronic excitations and the cubic term is due to lattice vibrations. Below the superconducting critical temperature this behavior is substantially altered. As the temperature drops below T_c (in zero magnetic field) the specific heat jumps to a higher value and then slowly decreases, eventually falling well below the value one would expect for a normal metal (Figure 34.6). By applying

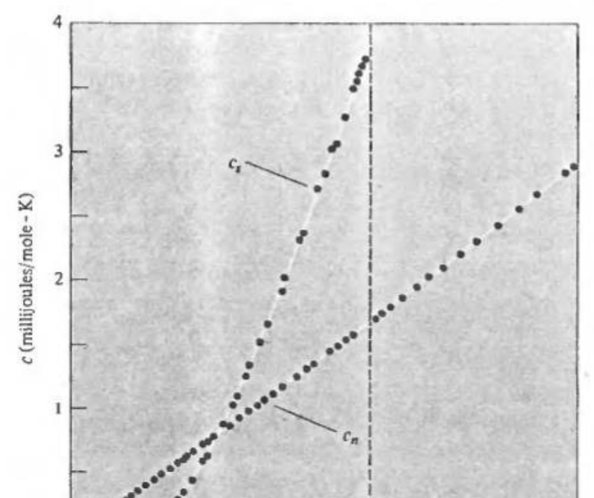

Figure 34.6
Low-temperature specific heat of normal and superconducting aluminum. The normal phase is produced below T_c by application of a weak (300-gauss) magnetic field, which destroys the superconducting ordering but has otherwise negligible effect on the specific heat. The Debye temperature is quite high in aluminum, so the specific heat is dominated by the electronic contribution throughout this temperature range (as can be seen from the fact that the normal-state curve is quite close to being linear). The discontinuity at T_c agrees well with the theoretical prediction (34.22) $[c_s - c_n]/c_n = 1.43$. Well below T_c, c_s drops far below c_n, suggesting the existence of an energy gap. (N. E. Phillips, *Phys. Rev.* **114**, 676 (1959).)

[20] The term "vortex" is often used to refer to the filaments themselves, as well as to the structure of the current in the vicinity of each filament. It can be shown that the magnetic flux enclosed by each vortex is just equal to the magnetic flux quantum, $hc/2e$ (see footnote 60).

a magnetic field to drive the metal into the normal state, one can compare the specific heats of the superconducting and normal states below the critical temperature.[21] Such an analysis reveals that in the superconducting state the linear electronic contribution to the specific heat is replaced by a term that vanishes much more rapidly at very low temperatures, having a dominant low-temperature behavior of the form $\exp(-\Delta/k_B T)$. This is the characteristic thermal behavior of a system whose excited levels are separated from the ground state by an energy 2Δ.[22] Both theory (see Eq. (34.19)) and experiment (see Table 34.3) indicate that the energy gap Δ is of order $k_B T_c$.

OTHER MANIFESTATIONS OF THE ENERGY GAP

Normal Tunneling

The conduction electrons in a superconductor and a normal metal can be brought into thermal equilibrium with one another by placing the metals into such close contact that they are separated only by a thin insulating layer,[23] which the electrons can cross by quantum-mechanical tunneling. In thermal equilibrium enough electrons have passed from one metal to the other to make the chemical potentials of electrons in both metals equal.[24] When both metals are normal, application of a potential difference then raises the chemical potential of one metal with respect to the other, and further electrons tunnel through the insulating layer. Such "tunneling currents" at normal metal junctions have been observed to obey Ohm's law. However, when one of the metals is a superconductor well below its critical temperature, then no current is observed to flow until the potential V reaches a threshold value, $eV = \Delta$ (see Figure 34.7). The size of Δ is in good agreement with the value inferred from low-temperature specific heat measurements, confirming the picture of a gap in the density of one-electron levels in the superconductor. As the temperature is raised toward T_c, the threshold voltage declines,[25] indicating that the energy gap itself is declining with increasing temperature.

Frequency Dependent Electromagnetic Behavior

The response of a metal to electromagnetic radiation (for example the transmission through thin films or the reflection from bulk samples) is determined by the frequency dependent conductivity. This in turn depends on the available mechanisms for energy absorption by the conduction electrons at the given frequency. Because the electronic excitation spectrum in the superconducting state is characterized by an energy gap Δ, one would expect the AC conductivity to differ substantially from its normal state form at frequencies small compared with $\Delta/\hbar$, and to be essentially the same in the superconducting and normal states at frequencies large compared with $\Delta/\hbar$. Except

[21] The normal specific heat is not appreciably affected by the presence of a magnetic field.

[22] See point 3, page 727.

[23] For example, the thin layer of oxide on the surfaces of the two specimens.

[24] See page 360.

[25] The threshold also becomes blurred, due to the presence of thermally excited electrons, which require less energy to tunnel.

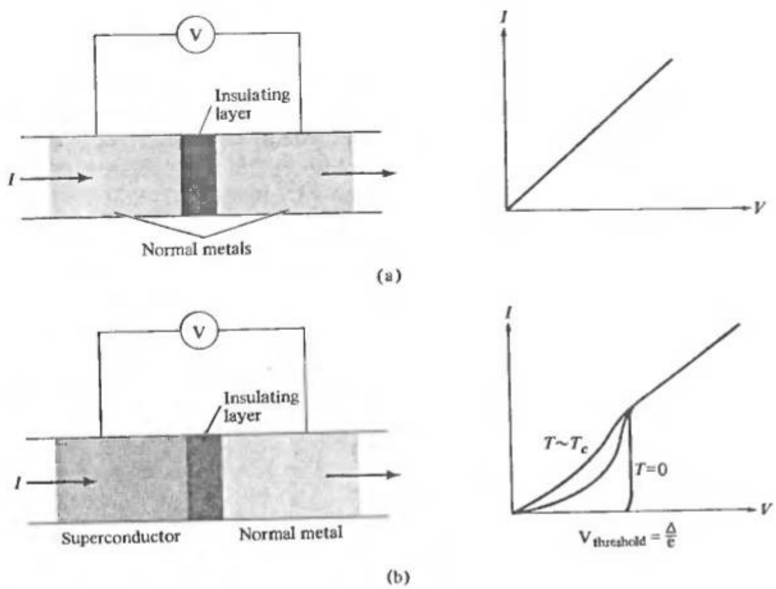

Figure 34.7
(a) Current-voltage relation for electron tunneling through a thin insulating barrier between two normal metals. For small currents and voltages the relation is linear. (b) Current-voltage relation for electron tunneling through a thin insulating barrier between a superconductor and a normal metal. The relation is strongly temperature-dependent. At $T = 0$ there is a sharp threshold, which is blurred at higher temperatures due to the thermal excitation of electrons across the energy gap within the superconductor.

quite near the critical temperature (see p. 744). $\Delta/\hbar$ is typically in the range between microwave and infrared frequencies. In the superconducting state an AC behavior is observed which is indistinguishable from that in the normal state at optical frequencies. Deviations from normal state behavior first appear in the infrared, and only at microwave frequencies does AC behavior fully displaying the lack of electronic absorption characteristic of an energy gap become completely developed.

Acoustic Attenuation

When a sound wave propagates through a metal the microscopic electric fields due to the displacement of the ions can impart energy to electrons near the Fermi level, thereby removing energy from the wave.[26] Well below T_c the rate of attenuation is markedly lower in a superconductor than a normal metal, as one would expect for sound waves, where $\hbar\omega < 2\Delta$.

[26] See pages 275–277.

THE LONDON EQUATION

F. London and H. London first examined in a quantitative way the fundamental fact that a metal in the superconducting state permits no magnetic field in its interior.[27] Their analysis starts with the two-fluid model of Gorter and Casimir.[28] The only crucial assumption of this model that we shall use is that in a superconductor at temperature $T < T_c$, only a fraction $n_s(T)/n$ of the total number of conduction electrons are capable of participating in a supercurrent. The quantity $n_s(T)$ is known as the density of superconducting electrons. It approaches the full electronic density n as T falls well below T_c, but it drops to zero as T rises to T_c. The remaining fraction of electrons are assumed to constitute a "normal fluid" of density $n - n_s$ that cannot carry an electric current without normal dissipation. The normal current and the supercurrent are assumed to flow in parallel; since the latter flows with no resistance whatever, it will carry the entire current induced by any small transitory electric field, and the normal electrons will remain quite inert. Normal electrons are therefore ignored in the discussion that follows.

Suppose that an electric field momentarily arises within a superconductor. The superconducting electrons will be freely accelerated without dissipation so that their mean velocity $\mathbf{v}_s$ will satisfy[29]

$$m \frac{d\mathbf{v}_s}{dt} = -e\mathbf{E}. \tag{34.1}$$

Since the current density carried by these electrons is $\mathbf{j} = -e\mathbf{v}_s n_s$, Eq. (34.1) can be written as

$$\frac{d}{dt}\mathbf{j} = \frac{n_s e^2}{m}\mathbf{E}. \tag{34.2}$$

Note that the Fourier transform of (34.2) gives the ordinary AC conductivity for an electron gas of density n_s in the Drude model, Eq. (1.29), when the relaxation time τ becomes infinitely large:

$$\begin{aligned} \mathbf{j}(\omega) &= \sigma(\omega)\mathbf{E}(\omega), \\ \sigma(\omega) &= i\frac{n_s e^2}{m\omega}. \end{aligned} \tag{34.3}$$

Substituting (34.2) into Faraday's law of induction,

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \tag{34.4}$$

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[27] F. London and H. London, *Proc. Roy. Soc.* (London), **A149**, 71 (1935), *Physica* **2**, 341 (1935); F. London, *Superfluids* vol. 1, Wiley, New York, 1954, and Dover, New York, 1954.

[28] The two-fluid model is also used to describe superfluid helium-4, and is described in both of the volumes by F. London, *Superfluids*, vols. 1 and 2, *Ibid.*

[29] We ignore band structure effects throughout this chapter and describe the electrons with free electron dynamics.

gives the following relation between current density and magnetic field:

$$\frac{\partial}{\partial t}\left(\nabla \times \mathbf{j} + \frac{n_s e^2}{mc}\mathbf{B}\right) = 0. \tag{34.5}$$

This relation, together with the Maxwell equation[30]

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j}, \tag{34.6}$$

determines the magnetic fields and current densities that can exist within a perfect conductor.

Note in particular that any static field $\mathbf{B}$ determines a static current density $\mathbf{j}$ through Eq. (34.6). Since any time-independent $\mathbf{B}$ and $\mathbf{j}$ are trivially solutions to (34.5), the two equations are consistent with an arbitrary static magnetic field. This is incompatible with the observed behavior of superconductors, which permit *no* fields in their interior. F. London and H. London discovered that this characteristic behavior of superconductors could be obtained by restricting the full set of solutions of (34.5) to those that obey[31]

$$\nabla \times \mathbf{j} = -\frac{n_s e^2}{mc}\mathbf{B}, \tag{34.7}$$

which is known as the London equation. Equation (34.5), which characterizes any medium that conducts electricity without dissipation, requires that $\nabla \times \mathbf{j} + (n_s e^2/mc)\mathbf{B}$ be independent of time; the more restrictive London equation, which specifically characterizes superconductors and distinguishes them from mere "perfect conductors," requires in addition that the time-independent value be zero.

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[30] We assume that the rate of time variation is so slow that the displacement current can be neglected. We also take the field in (34.6) to be $\mathbf{B}$ rather than $\mathbf{H}$; this is because $\mathbf{j}$ represents the mean *microscopic* current flowing in the superconductor. The field $\mathbf{H}$ would appear only if we represented $\mathbf{j}$ by an effective magnetization density satisfying $\nabla \times \mathbf{M} = \mathbf{j}/c$, and defined $\mathbf{H}$ in the usual way as $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$. In that case Eq. (34.6) would be replaced by the equation $\nabla \times \mathbf{H} = 0$. Given the definitions of $\mathbf{H}$ and $\mathbf{M}$, this would be a completely equivalent formulation.

[31] This is a local relation; i.e., the current at the point $\mathbf{r}$ is related to the field at the same point. A. B. Pippard pointed out that, more generally, the current at $\mathbf{r}$ should be determined by the field within a neighborhood of the point $\mathbf{r}$ according to a relation of the form

$$\nabla \times \mathbf{j}(\mathbf{r}) = -\int d\mathbf{r}'\, K(\mathbf{r} - \mathbf{r}')\mathbf{B}(\mathbf{r}'),$$

where the kernel $K(\mathbf{r})$ is appreciable only for r less than a length ξ_0. The distance ξ_0 is one of several fundamental lengths characterizing a superconductor, all of which, unfortunately, are indiscriminately referred to as "the coherence length." In pure materials well below the critical temperature all such coherence lengths are the same, but near T_c or in materials with short impurity mean free paths, the "coherence length" may vary from one context to another. We shall avoid this tangle of coherence lengths by restricting our comments on its significance to the low-temperature pure case, where all coherence lengths agree. It turns out that in such cases the criterion for whether a superconductor is type I or type II is that the coherence length be large (type I) or small (type II) compared with the London penetration depth Λ (Eq. (34.9)).

The reason for replacing (34.5) by the more restrictive London equation is that the latter leads directly to the Meissner effect.[32] Equations (34.6) and (34.7) imply that

$$\nabla^2\mathbf{B} = \frac{4\pi n_s e^2}{mc^2}\,\mathbf{B},$$
$$\nabla^2\mathbf{j} = \frac{4\pi n_s e^2}{mc^2}\,\mathbf{j}. \tag{34.8}$$

These equations, in turn, predict that currents and magnetic fields in superconductors can exist only within a layer of thickness Λ of the surface, where Λ, known as the London penetration depth, is given by[33]

$$\Lambda = \left(\frac{mc^2}{4\pi n_s e^2}\right)^{1/2} = 41.9\left(\frac{r_s}{a_0}\right)^{3/2}\left(\frac{n}{n_s}\right)^{1/2}\text{Å}. \tag{34.9}$$

Thus the London equation implies the Meissner effect, along with a specific picture of the surface currents that screen out the applied field. These currents occur within a surface layer of thickness 10^2–10^3 Å (well below T_c—the thickness can be considerably greater near the critical temperature, where n_s approaches zero). Within this same surface layer the field drops continuously to zero. These predictions are confirmed by the fact that the field penetration is not complete in superconducting films as thin as or thinner than the penetration depth Λ.

MICROSCOPIC THEORY: QUALITATIVE FEATURES

The microscopic theory of superconductivity was put forth by Bardeen, Cooper, and Schrieffer in 1957.[34] In a broad survey such as this we cannot develop the formalism necessary for an adequate description of their theory, and can only describe in a qualitative way the underlying physical principles and the major theoretical predictions.

The theory of superconductivity requires, to begin with, a net *attractive* interaction between electrons in the neighborhood of the Fermi surface. Although the direct electrostatic interaction is repulsive, it is possible for the ionic motion to "overscreen" the Coulomb interaction, leading to a net attraction.[35] We described this possibility

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[32] We shall see below that the London equation is also suggested by certain features of the microscopic electronic ordering.

[33] Consider, for example, the case of a semiinfinite superconductor occupying the half space $x > 0$. Then Eq. (34.8) implies that the physical solutions decay exponentially:

$$B(x) = B(0)e^{-x/\Lambda}.$$

Other geometries are examined in Problem 2.

[34] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957). The theory is generally referred to as the BCS theory.

[35] Direct evidence that the ionic motion plays a role in establishing superconductivity is provided by the *isotope effect*: The critical temperature of different isotopes of a given metallic element varies from one isotope to another, frequently (but not always) as the inverse square root of the ionic mass. The fact that there is any dependence on ionic mass demonstrates that the ions cannot play a merely static role in the transition, but must be dynamically involved.

in Chapter 26, where we found, in a simplified model, that allowing the ions to move in response to motions of the electrons led to a net interaction between electrons with wave vectors **k** and **k**′ of the form[36]

$$v^{\text{eff}}_{\mathbf{k}\mathbf{k}'}(\mathbf{k}, \mathbf{k}') = \frac{4\pi e^2}{q^2 + k_0{}^2} \cdot \frac{\omega^2}{\omega^2 - \omega_{\mathbf{q}}{}^2}, \tag{34.10}$$

where $\hbar\omega$ is the difference in electronic energies, k_0 is the Thomas-Fermi wave vector (17.50), **q** is the difference in electron wave vectors, and $\omega_{\mathbf{q}}$ is the frequency of a phonon of wave vector **q**.

Thus screening by the ionic motion can yield a net attractive interaction between electrons with energies sufficiently close together (roughly, separated by less than $\hbar\omega_D$, a measure of the typical phonon energy). This attraction[37] underlies the theory of superconductivity.

Given that electrons whose energies differ by $O(\hbar\omega_D)$ can experience a net attraction, the possibility arises that such electrons might form bound pairs.[38] This would appear to be doubtful, since in three dimensions two particles must interact with a certain minimum strength to form a bound state, a condition that the rather limited effective attraction would be unlikely to meet. However, Cooper[39] argued that this apparently implausible possibility was made quite likely by the influence of the remaining $N - 2$ electrons on the interacting pair, through the Pauli exclusion principle.

Cooper considered the problem of two electrons with an attractive interaction that would be far too weak to bind them if they were in isolation. He demonstrated, however, that in the presence of a Fermi sphere of additional electrons[40] the exclusion principle radically altered the two-electron problem so that a bound state existed no matter how weak the attraction. Aside from indicating that the net attraction need not have a minimum strength to bind a pair, Cooper's calculation also indicated how the superconducting transition temperature could be so low compared with all other characteristic temperatures of the solid. This followed from the form of his solution, which gave a binding energy that was very small compared with the potential energy of attraction when the attraction was weak.

Cooper's argument applies to a single pair of electrons in the presence of a normal Fermi distribution of additional electrons. The theory of Bardeen, Cooper, and

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[36] See pages 518–519. That such an attraction was possible and might be the source of superconductivity was first emphasized by H. Fröhlich.

[37] Any other mechanism leading to a net attractive interaction between electrons near the Fermi surface would also lead to a superconducting state at low enough temperature. However, no cases of superconductivity due to other mechanisms have been convincingly established in metals.

[38] More generally, one might inquire into the possibility of n electrons binding together, but the weak interaction and the Pauli exclusion principle make the case $n = 2$ the most promising.

[39] L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).

[40] The degenerate Fermi distribution of additional electrons was taken to play no role other than prohibiting the two electrons from occupying any levels with wave vectors less than k_F. Thus the Cooper calculation was basically a two-electron calculation except that analysis was restricted to states built out of one-electron levels from which all plane waves with wave vectors less than k_F had been excluded. See Problem 4.

Schrieffer took an essential further step, constructing a ground state in which *all* electrons form bound pairs. This is a considerable extension of the Cooper model, for each electron now plays two roles: It provides the necessary restriction on allowed wave vectors (via the exclusion principle) that makes possible the binding of other pairs in spite of the weakness of the attraction; at the same time, the electron itself is participating in one of the bound pairs.

The BCS approximation to the electronic ground state wave function can be described as follows: Group the N conduction electrons into $N/2$ pairs[41] and let each pair be described by a bound-state wave function $\phi(\mathbf{r}s, \mathbf{r}'s')$, where $\mathbf{r}$ is the electronic position and s is the spin quantum number. Then consider the N-electron wave function that is just the product of $N/2$ *identical* such two-electron wave functions:

$$\Psi(\mathbf{r}_1 s_1, \ldots, \mathbf{r}_N s_N) = \phi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2) \ldots \phi(\mathbf{r}_{N-1} s_{N-1}, \mathbf{r}_N s_N). \tag{34.11}$$

This describes a state in which all electrons are bound, in pairs, into identical two-electron states. However, it lacks the symmetry required by the Pauli principle. To construct a state that changes sign whenever the space and spin coordinates of any two electrons are interchanged, we must antisymmetrize the state (34.11). This leads to the BCS ground state:[42]

$$\Psi_{\text{BCS}} = \mathcal{A}\Psi. \tag{34.12}$$

It may seem surprising that the state (34.12) satisfies the Pauli principle even though all the pair wave functions ϕ appearing in it are identical. Indeed, if we had constructed a product state analogous to (34.11) out of N identical *one*-electron levels, subsequent antisymmetrization would cause it to vanish. The fundamental requirement of antisymmetry implies that no one-electron level can be doubly occupied when the states are antisymmetrized products of one-electron levels. However, the requirement of antisymmetry does not imply a corresponding restriction on the occupancy of two-electron levels in states that are antisymmetrized products of two-electron levels.[43]

It can be demonstrated that if the state (34.12) is taken as a trial state in a variational estimate of the ground-state energy, then the optimum choice of ϕ must lead to a lower energy than the best choice of Slater determinants (i.e., the best independent electron trial function) for any attractive interaction, no matter how weak.

In the BCS theory the pair wave functions ϕ are taken to be singlet states;[44] i.e.,

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[41] The odd electron (if N is odd) is of no significance in the limit of a large system.

[42] The antisymmetrizer $\mathcal{A}$ simply adds to the function it acts upon each of the $N! - 1$ other functions obtained by all possible permutations of the arguments, weighted with $+1$ or -1 according to whether the permutation is constructed out of an even or odd number of pair interchanges.

[43] This is why it is possible for a pair of fermions to behave statistically like a boson. Indeed, if the binding energy of each pair were so strong that the size of the pair were small compared with the interparticle spacing r_s, then the ground state would consist of $N/2$ bosons, all condensed into the same two-electron level. As we shall see, however, the size of a Cooper pair is large compared with r_s, and it can be highly misleading to view the Cooper pairs as independent bosons.

[44] If the pair states were triplets (spin 1) this would imply characteristic magnetic properties that are not observed. Triplet pairing has, however, been observed in liquid helium-3, a degenerate Fermi liquid that bears many resemblances to the electron gas in metals. See, for example, *Nobel Symposium* 24, *Collective Properties of Physical Systems*, B. Lundqvist and S. Lundqvist, eds., Academic Press, New York, 1973, pages 84–120.

the two electrons in the pair have opposite spin and the orbital part of the wave function, $\phi(\mathbf{r}, \mathbf{r}')$ is symmetric. If the pair state is chosen to be translationally invariant (ignoring possible complications due to the periodic potential of the lattice) so that $\phi(\mathbf{r}, \mathbf{r}')$ has the form $\chi(\mathbf{r} - \mathbf{r}')$, then one can write:

$$\chi(\mathbf{r} - \mathbf{r}') = \frac{1}{V} \sum_{\mathbf{k}} \chi_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}'}. \tag{34.13}$$

Thus χ can be viewed as a superposition of products of one-electron levels in each term of which electrons with equal and opposite wave vectors are paired.[45]

One result of the variational calculation of Ψ_{BCS} is that the spatial range ξ_0 of the pair wave function[46] is very large compared with the spacing between electrons r_s. A crude estimate of ξ_0 can be constructed as follows: The pair wave function $\phi(\mathbf{r})$ is presumably a superposition of one-electron levels with energies within $O(\Delta)$ of $\mathcal{E}_F$, since outside of that energy range tunneling experiments indicate that the one-electron level density is little altered from the form it has in a normal metal. The spread in momenta of the one-electron levels making up the pair state is therefore fixed by the condition

$$\Delta = \delta\mathcal{E} = \delta\left(\frac{p^2}{2m}\right) = \left(\frac{p_F}{m}\right)\delta p \approx v_F\,\delta p. \tag{34.14}$$

The spatial range of $\phi(\mathbf{r})$ is thus of order

$$\xi_0 \sim \frac{\hbar}{\delta p} \sim \frac{\hbar v_F}{\Delta} \sim \frac{1}{k_F}\frac{\mathcal{E}_F}{\Delta}. \tag{34.15}$$

Since $\mathcal{E}_F$ is typically 10^3–10^4 times Δ, and k_F is of order $10^8\ \text{cm}^{-1}$, ξ_0 is typically 10^3 Å.

Thus within the region occupied by any given pair will be found the centers of many (millions, or more) pairs. This is a very crucial feature of the superconducting state: The pairs cannot be thought of as independent particles, but are spatially interlocked in a very intricate manner, which is essential to the stability of the state.

The above description summarizes the essential features of the electronic ground state in a superconductor. To describe the excited states, or the thermal or transport properties of a superconductor, one must resort to more sophisticated formalisms. We shall not go into these here, except to emphasize that the underlying physical picture remains that of a system of paired electrons. In nonequilibrium processes the pair state can be more complex. At nonzero temperatures a fraction of the pairs are thermally dissociated, and the density of superconducting electrons n_s is determined by the fraction that remain paired. Furthermore, because of the intricate self-consistent nature of the pairing, the thermal dissociation of some of the pairs at nonzero

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[45] This aspect of the ground state is often emphasized, and the assertion is made that electrons with opposite spins and wave vectors are bound in pairs. This is no more (or less) accurate than the assertion that any translationally invariant bound state of two identical particles pairs them with equal and opposite momenta; i.e., the assertion correctly focuses attention on the fact that the total momentum of the bound pair is zero, but it misleadingly distracts attention from the fact that the state is a superposition of such pairs, and therefore localized in the relative position coordinate (unlike a single product of plane waves).

[46] In pure superconductors well below T_c this turns out to be the same as the coherence length, described in footnote 31. It is therefore denoted by the same symbol.

temperatures results in a temperature dependence in the characteristic properties (for example, the range of the pair function) of those pairs that remain bound. As T rises through T_c all pairs become dissociated, and the ground state reverts continuously back to the normal ground state of the independent electron approximation.

QUANTITATIVE PREDICTIONS OF THE ELEMENTARY MICROSCOPIC THEORY

In its simplest form the BCS theory makes two gross oversimplifications in the basic Hamiltonian that describes the conduction electrons:

1. The conduction electrons are treated in the free electron approximation; band structure effects are ignored.
2. The rather complicated net attractive interaction[47] (34.10) between electrons near the Fermi energy is further simplified to an effective interaction V. The matrix element of V between a two-electron state with electronic wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, and another with wave vectors $\mathbf{k}_3$ and $\mathbf{k}_4$, is taken in a volume Ω to be

$$\begin{aligned} \langle \mathbf{k}_1\mathbf{k}_2|V|\mathbf{k}_3\mathbf{k}_4\rangle &= -V_0/\Omega, \text{ when } \mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{k}_4, \\ &\qquad |\mathcal{E}(\mathbf{k}_i) - \mathcal{E}_F| < \hbar\omega,\ i = 1, \ldots, 4, \\ &= 0, \text{ otherwise.} \end{aligned} \tag{34.16}$$

The restriction on wave vectors is required for any translationally invariant potential; the significant aspect of the interaction (34.16) is the attraction experienced whenever all four free electron energies are within an amount $\hbar\omega$ (usually taken to be of order $\hbar\omega_D$) of the Fermi energy.

Equation (34.16) is a gross oversimplification of the actual net interaction, and any results depending on its detailed features are to be viewed with suspicion. Fortunately, the theory predicts a number of relations from which the two phenomenological parameters V_0 and $\hbar\omega$ are absent. These relations are rather well obeyed by a large class of superconductors, with certain notable exceptions (such as lead and mercury). Even these exceptions, known as "strong coupling superconductors" have been convincingly brought into the more general framework of the BCS theory, provided that the simplifications inherent in the approximate interaction (34.16) are abandoned, along with certain other overly simple representations of the effects of phonons.[48]

From the model Hamiltonian (34.16), the BCS theory deduces the following major equilibrium predictions:

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[47] One must not forget that even Eq. (34.10) is a comparatively crude representation of the detailed dynamic interaction induced among the electrons by the phonons. In so-called strong coupling superconductors (see below) even Eq. (34.10) is inadequate.

[48] In the theory of strong-coupling superconductors one treats the full electron-phonon system, without at the start trying to eliminate the phonons in favor of an effective interaction of the form (34.16), or even (34.10). As a result, the net interaction between electrons is more complicated and no longer instantaneous but retarded. Furthermore, the lifetimes due to electron-phonon scattering of the electronic levels within $\hbar\omega_D$ from the Fermi level may be so short that the picture of well-defined one-electron levels out of which pairs are formed also requires modification.

Critical Temperature

In zero magnetic field, superconducting ordering sets in at a critical temperature given by

$$k_B T_c = 1.13 \hbar\omega e^{-1/N_0 V_0}, \tag{34.17}$$

where N_0 is the density of electronic levels for a single spin population in the normal metal[49] and ω and V_0 are the parameters of the model Hamiltonian (34.16). Because of the exponential dependence, the effective coupling V_0 cannot be determined precisely enough to permit very accurate computations of the critical temperature from (34.17). However, this same exponential dependence accounts for the very low critical temperatures (typically one to three orders of magnitude below the Debye temperature), for although $\hbar\omega$ is of order $k_B\Theta_D$, the strong dependence on N_0V_0 can lead to the observed range of critical temperatures with N_0V_0 in the range from 0.1 to 0.5, i.e., with $V_0 n$ in the range[50] $0.1\mathcal{E}_F$ to $0.5\mathcal{E}_F$. Note also that no matter how weak the coupling V_0, the theory predicts a transition, though the transition temperature (34.17) may be unobservably low.

Energy Gap

A formula similar to (34.17) is predicted for the zero-temperature energy gap:

$$\Delta(0) = 2\hbar\omega e^{-1/N_0 V_0}. \tag{34.18}$$

The ratio of (34.18) to (34.17) gives a fundamental formula independent of the phenomenological parameters:

$$\frac{\Delta(0)}{k_B T_c} = 1.76. \tag{34.19}$$

This result appears to hold for a large number of superconductors to within about 10 percent (Table 34.3). Those for which it fails (for example, lead and mercury, where the discrepancy is closer to 30 percent) tend systematically to deviate from other predictions of the simple theory as well, and can be brought closer into line with theoretical predictions by using the more elaborate analysis of the strong-coupling theory.

The elementary theory also predicts that near the critical temperature (in zero field) the energy gap vanishes according to the universal law[51]

$$\frac{\Delta(T)}{\Delta(0)} = 1.74\left(1 - \frac{T}{T_c}\right)^{1/2}, \qquad T \approx T_c. \tag{34.20}$$

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[49] The quantity N_0 is simply $g(\mathcal{E}_F)/2$. This notation for the density of levels is widely used in the literature of superconductivity.

[50] The quantity N_0 is of order $n/\mathcal{E}_F$. See Eq. (2.65).

[51] Equation (34.20) is a characteristic result of mean field theory (cf. the prediction of mean field theory that the spontaneous magnetization vanishes as $(T_c - T)^{1/2}$, Chapter 33, Problem 6). Mean field theory is known to be wrong in ferromagnets sufficiently near the critical temperature. Presumably it fails sufficiently near T_c in a superconductor as well, but arguments have been advanced that the region inside of which mean field theory fails is exceedingly small (typically $(T_c - T)/T_c \approx 10^{-8}$). Superconductors provide a rare example of a phase transition that is well described by a mean field theory quite near the critical point.

Table 34.3
MEASURED VALUES[a] OF $2\Delta(0)/k_B T_c$

ELEMENT	$2\Delta(0)/k_B T_c$
Al	3.4
Cd	3.2
Hg (α)	4.6
In	3.6
Nb	3.8
Pb	4.3
Sn	3.5
Ta	3.6
Tl	3.6
V	3.4
Zn	3.2

[a] $\Delta(0)$ is taken from tunneling experiments. Note that the BCS value for this ratio is 3.53. Most of the values listed have an uncertainty of ± 0.1.

Source: R. Mersevey and B. B. Schwartz, *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969.

Critical Field

The elementary BCS prediction for $H_c(T)$ is often expressed in terms of the deviation from the empirical law:[52]

$$\frac{H_c(T)}{H_c(0)} \approx 1 - \left(\frac{T}{T_c}\right)^2. \tag{34.21}$$

The quantity $[H_c(T)/H_c(0)] - [1 - (T/T_c)^2]$ is shown for several superconductors in Figure 34.8, along with the BCS prediction. The departure is small in all cases, but note that the strong-coupling superconductors lead and mercury are more out of line than the others.

Specific Heat

At the critical temperature (in zero magnetic field) the elementary BCS theory predicts a discontinuity in the specific heat that can also be put in a form independent of the parameters in the model Hamiltonian (34.16):[53]

$$\left.\frac{c_s - c_n}{c_n}\right|_{T_c} = 1.43. \tag{34.22}$$

[52] The BCS prediction can again be cast in a parameter independent form. At low temperatures it is $H_c(T)/H_c(0) \approx 1 - 1.06(T/T_c)^2$, while near T_c it is $H_c(T)/H_c(0) = 1.74[1 - (T/T_c)]$.

[53] A specific heat discontinuity at T_c is also a characteristic mean field theory result. Presumably, *very* close to T_c the specific heat may diverge.

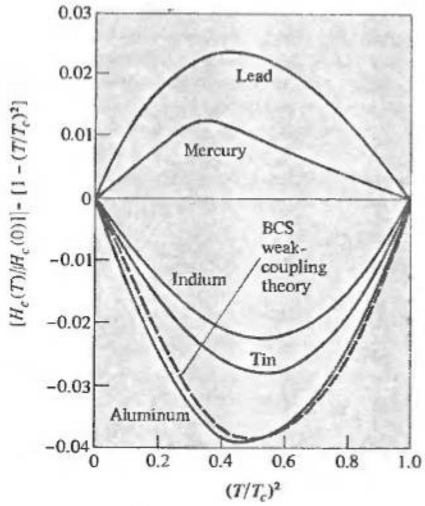

Figure 34.8
The deviation from the crude empirical relation $H_c(T)/H_c(0) \approx 1 - [T/T_c]^2$, as measured in several metals and as predicted by the simple BCS theory. Deviations from the simple BCS prediction are more pronounced in the "strong-coupling" superconductors, lead and mercury. (J. C. Swihart et al., *Phys. Rev. Lett.* 14, 106 (1965).)

The agreement of this prediction with experiment is again good to about 10 percent except for the strong-coupling superconductors (Table 34.4).

The low-temperature electronic specific heat can also be cast in a parameter independent form,

$$\frac{c_s}{\gamma T_c} = 1.34\left(\frac{\Delta(0)}{T}\right)^{3/2} e^{-\Delta(0)/T}, \tag{34.23}$$

where γ is the coefficient of the linear term in the specific heat of the metal in the normal state (Eq. (2.80)). Note the exponential drop, on a scale determined by the energy gap $\Delta(0)$.

MICROSCOPIC THEORY AND THE MEISSNER EFFECT

In the presence of a magnetic field, diamagnetic currents will flow in the equilibrium state of a metal, whether it is normal or superconducting, although the currents are vastly greater in a superconductor. In a free electron model the current will be determined to first order in the field by an equation of the form[54]

$$\nabla \times \mathbf{j}(\mathbf{r}) = -\int d\mathbf{r}'\, K(\mathbf{r} - \mathbf{r}')\mathbf{B}(\mathbf{r}'). \tag{34.24}$$

If it happens that the kernel $K(\mathbf{r})$ satisfies

$$\int d\mathbf{r}\, K(\mathbf{r}) = K_0 \neq 0, \tag{34.25}$$

then in the limit of magnetic fields that vary slowly over the range of $K(\mathbf{r})$, Eq. (34.24) reduces to

$$\nabla \times \mathbf{j}(\mathbf{r}) = -K_0\mathbf{B}(\mathbf{r}), \tag{34.26}$$

[54] This is the same kernel K mentioned in footnote 31.

Table 34.4
MEASURED VALUES OF THE RATIO[a]
$[(c_s - c_n)/c_n]_{T_c}$

ELEMENT	$\left[\dfrac{c_s - c_n}{c_n}\right]_{T_c}$
Al	1.4
Cd	1.4
Ga	1.4
Hg	2.4
In	1.7
La (HCP)	1.5
Nb	1.9
Pb	2.7
Sn	1.6
Ta	1.6
Tl	1.5
V	1.5
Zn	1.3

[a] The simple BCS prediction is $[(c_s - c_n)/c_n]_{T_c} = 1.43$.
Source: R. Mersevey and B. B. Schwartz, *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969.

which is nothing but the London equation (34.7), with n_s given by

$$n_s = \frac{mc}{e^2} K_0. \tag{34.27}$$

Since the London equation implies the Meissner effect, it follows that in normal metals the constant K_0 must vanish. To demonstrate that BCS theory implies the Meissner effect, one calculates the kernel $K(\mathbf{r})$ by perturbation theory in the applied field, and verifies explicitly that $K_0 \neq 0$.

The actual demonstration that $K_0 \neq 0$ is a fairly complex application of BCS theory. However, a more intuitive explanation for the London equation was offered at the time the equation was first put forth, by the Londons. This explanation can be made somewhat more compelling through a phenomenological theory of V. L. Ginzburg and L. D. Landau,[55] which, though proposed seven years prior to the BCS theory, can be quite naturally described in terms of some of the fundamental notions of the microscopic theory.

THE GINZBURG-LANDAU THEORY

Ginzburg and Landau asserted that the superconducting state could be characterized by a complex "order parameter" $\psi(\mathbf{r})$, which vanishes above T_c and whose

[55] V. L. Ginzburg and L. D. Landau, *Zh. Eksp. Teor. Fiz.* **20**, 1064 (1950).

magnitude measures the degree of superconducting order at position $\mathbf{r}$ below T_c.[56] From the perspective of the BCS theory the order parameter can be viewed as a one-particle wave function describing the position of the center of mass of a Cooper pair. Since all Cooper pairs are in the same two-electron state, a single function suffices. Because the order parameter does not refer to the relative coordinate of the two electrons in the pair, the description of a superconductor in terms of $\psi(\mathbf{r})$ is valid only for phenomena that vary slowly on the scale[57] of the dimensions of the pair.

In the ground state of the superconductor each pair is in a translationally invariant state that does not depend on the center of mass coordinate; i.e., the order parameter is a constant. The order parameter develops interesting structure when currents flow, or when an applied field appears. A fundamental assumption of the Ginzburg-Landau theory is that the current flowing in a superconductor characterized by order parameter $\psi(\mathbf{r})$ in the presence of a magnetic field given by the vector potential $\mathbf{A}(\mathbf{r})$ is given by the ordinary quantum-mechanical formula for the current due to a particle of charge $-2e$ and mass $2m$ (i.e., the Cooper pair itself) described by a wave function $\psi(\mathbf{r})$, namely

$$\mathbf{j} = -\frac{e}{2m}\left[\psi^* \left\{\left(\frac{\hbar}{i}\nabla + \frac{2e}{c}\mathbf{A}\right)\psi\right\} + \left\{\left(\frac{\hbar}{i}\nabla + \frac{2e}{c}\mathbf{A}\right)\psi\right\}^* \psi\right]. \tag{34.28}$$

The London equation (34.7) follows from (34.28), provided one also assumes that the significant spatial variation of the order parameter $\psi = |\psi|e^{i\phi}$ is through the phase ϕ, and not the magnitude $|\psi|$. Since the magnitude of the order parameter measures the degree of superconducting ordering, this assumption restricts consideration to disturbances in which the density of Cooper pairs is not appreciably altered from its uniform thermal equilibrium value. This should be the case in phenomena in which the pairs can flow, but not accumulate or be destroyed.[58]

Given this assumption, the relation (34.28) for the current simplifies to

$$\mathbf{j} = -\left[\frac{2e^2}{mc}\mathbf{A} + \frac{e\hbar}{m}\nabla\phi\right]|\psi|^2. \tag{34.29}$$

[56] It is sometimes helpful to bear in mind an analogy to a Heisenberg ferromagnet, where the order parameter may be viewed as the mean value of the local spin $\mathbf{s}(\mathbf{r})$. Above T_c, $\mathbf{s}(\mathbf{r})$ vanishes; below, it gives the local value of the spontaneous magnetization. In the ground state $\mathbf{s}(\mathbf{r})$ is independent of $\mathbf{r}$ (and, correspondingly, in a uniform superconductor that carries no current, $\psi(\mathbf{r})$ is constant). However, one can consider more complicated configurations of the ferromagnet, in which, for example, the magnetization is constrained by applied fields to point in different directions at two ends of a bar. A position-dependent $\mathbf{s}(\mathbf{r})$ is also useful in investigating aspects of domain structure. In a similar way, a position-dependent $\psi(\mathbf{r})$ is used to investigate current-carrying configurations of a superconductor.

[57] Well below T_c this is just the length ξ_0, described on page 742.

[58] More generally, when the degree of superconducting order does have significant spatial variation, one must use a second Ginzburg-Landau equation in conjunction with (34.28) to determine both ψ and the current. The second equation relates the spatial rate of change of the order parameter to the vector potential, and bears a (to some extent deceptive) resemblance to a one-particle Schrödinger equation. The use of the full set of Ginzburg-Landau equations is essential, for example, in the description of vortices in type II superconductors, for in the core of the vortex the magnitude of the order parameter drops rapidly to zero, yielding a region in which the magnetic flux is appreciable.

Since the curl of any gradient vanishes, and since $|\psi|^2$ is essentially constant, we immediately deduce the London equation (34.7) provided that we identify the superfluid density n_s with $2|\psi|^2$, which is reasonable in view of the interpretation of ψ as a wave function characterizing particles of charge $2e$.

FLUX QUANTIZATION

Equation (34.29) has an even more striking implication than the London equation. Consider a superconductor in the shape of a ring (Figure 34.9). If we integrate (34.29)

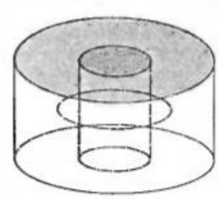

Figure 34.9
A ring of superconducting material, showing a path encircling the aperture and lying well within the interior of the superconductor.

over a path deep inside the superconducting material enclosing the hole in the ring, then, since appreciable currents can flow only near the surface of the superconductor, we find that

$$0 = \oint \mathbf{j} \cdot d\boldsymbol{\ell} = \oint \left(\frac{2e^2}{mc} \mathbf{A} + \frac{e\hbar}{m} \nabla \phi \right) \cdot d\boldsymbol{\ell}. \tag{34.30}$$

Stokes theorem gives

$$\int \mathbf{A} \cdot d\boldsymbol{\ell} = \int \nabla \times \mathbf{A} \cdot d\mathbf{S} = \int \mathbf{B} \cdot d\mathbf{S} = \Phi, \tag{34.31}$$

where Φ is the flux enclosed by the ring.[59] Furthermore, since the order parameter is single-valued, its phase must change by 2π times an integer n when the ring is encircled:

$$\oint \nabla \phi \cdot d\boldsymbol{\ell} = \Delta \phi = 2\pi n. \tag{34.32}$$

Combining these results, we conclude that the magnetic flux enclosed by the ring must be quantized:

$$|\Phi| = \frac{nhc}{2e} = n\Phi_0. \tag{34.33}$$

The quantity $\Phi_0 = hc/2e = 2.0679 \times 10^{-7}$ gauss-cm^2 is known as the fluxoid, or flux quantum. Flux quantization has been observed and is one of the most compelling pieces of evidence for the validity of the description of a superconductor by means of a complex order parameter.[60]

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[59] Since the magnetic field cannot penetrate the superconducting material, the enclosed flux will not depend on the choice of path, as long as the path is deep inside the material.

[60] B. S. Deaver and W. M. Fairbank, *Phys. Rev. Lett.* 7, 43 (1961); R. Doll and M. Näbauer, *Phys. Rev. Lett.* 7, 51 (1961). The Ginzburg-Landau theory also predicts, and experiments have confirmed, that each vortex in a type II superconductor contains a single quantum of magnetic flux.

MICROSCOPIC THEORY AND PERSISTENT CURRENTS

The property for which superconductors are named is unfortunately one of the most difficult to extract from the microscopic theory. In a sense perfect conductivity is implied by the Meissner effect, for macroscopic currents must flow without dissipation in order to screen macroscopic magnetic fields in equilibrium. Indeed, the direct microscopic derivation of persistent currents is not dissimilar to that of the Meissner effect. One calculates to linear order the current induced by an electric field, and demonstrates that there is a piece in the AC conductivity that has the form (34.3) appropriate to an electron gas without dissipation. For this it suffices to prove that[61]

$$\lim_{\omega \to 0} \omega \operatorname{Im} \sigma(\omega) \neq 0. \tag{34.34}$$

The value of the nonzero constant determines, by comparison with (34.3), the value of the density of superconducting electrons n_s.

Demonstrating that (34.34) holds is more complicated than demonstrating the condition (34.25) for the Meissner effect, because it is essential to include the effects of scattering: If there were no scattering any metal would obey (34.34), but even in the absence of scattering a calculation of diamagnetism in a normal metal reveals no Meissner effect. However, the calculation has been done[62] and the value of n_s deduced from the low-frequency conductivity is found to agree with that deduced from the calculation of the Meissner effect. The calculation is unfortunately quite formal, and does not provide any intuitive explanation for the remarkable fact that none of the familiar scattering mechanisms are effective in degrading a current, once it has been established in a superconducting metal. Such an intuitive explanation is at least suggested by the following line of reasoning:[63]

Suppose that we use an electric field to establish a current in a metal, and then turn off the field and ask how the current can decay. In a normal metal the current can be degraded one electron at a time; i.e., scattering processes can reduce the total momentum of the electronic system by a series of collisions of individual electrons with impurities, phonons, imperfections, etc., each of which, on the average, drives the momentum distribution back to its equilibrium form, in which the total current vanishes. When a current is established in a superconductor, all the Cooper pairs move together: The single two-electron state describing each of the pairs is one with

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[61] Equation (34.34) is not dissimilar in structure to the condition (34.25) for a Meissner effect. The integral over all space of the kernel K is equal to the $k = 0$ limit of its spatial Fourier transform. In both cases one must establish the failure of a certain electromagnetic response function to vanish, in an appropriate long-wavelength or low-frequency limit.

[62] See, for example, A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, Englewood Cliffs, N.J., 1963, pp. 334–341.

[63] A variety of "intuitive" arguments have been offered on this point, many of them quite spurious. There is, for example, an argument (based on an old argument of Landau's to explain superfluidity in ^{4}He) purporting to deduce persistent currents from the existence of a gap in the one-electron excitation spectrum. But this merely explains why currents cannot be degraded by one-electron excitations, leaving open the possibility of degrading the current pair by pair. The argument we indicate here can be found under many guises, associated with the notions of "rigidity of the wave function," "off-diagonal long-range order," or "long-range phase coherence."

a nonzero center of mass momentum.[64] One might expect that such a current could be degraded by single-pair collisions, analogous to the one-electron collisions in a normal metal, in which individual pairs have their center of mass momenta reduced back to zero by collisions. Such a suggestion, however, fails to take into account the delicate interdependence of the pairs.[65] Essential to the stability of the paired state is the fact that all the other pairs exist and are described by identical pair wave functions. Thus one cannot change the pair wave functions individually without destroying the paired state altogether, at an enormous cost in free energy.

The supercurrent-degrading transition that is least costly in free energy depends, in general, on the geometry of the specimen, but it usually requires destruction of the pairing in some macroscopic portion of the sample. Such processes are possible, but the cost in free energy will in general be so large that the lifetime of the supercurrent is infinite on any practical time scale.[66]

SUPERCURRENT TUNNELING; THE JOSEPHSON EFFECTS

We have described (page 735) the tunneling of single electrons from a superconducting metal through a thin insulating barrier into a normal metal, and indicated how measurements of the tunneling current give information about the density of one-electron levels in the superconductor. Measurements can also be made of the tunneling currents when both metals are superconductors, and the results are fitted well by assuming that both metals have one-electron-level densities of the form predicted by the BCS theory (Figure 34.10). In 1962 Josephson[67] predicted that in addition to this "normal tunneling" of single electrons there should be another component to the tunneling current carried by paired electrons: Provided that the barrier is not too thick, electron pairs can traverse the junction from one superconductor to the other without dissociating.

One immediate consequence of this observation is that a supercurrent of pairs should flow across the junction in the absence of any applied electric field (the DC Josephson effect). Because the two superconductors are only weakly coupled (i.e., because the paired electrons must cross a gap of nonsuperconducting material), the typical tunneling current across the junction will be far smaller than typical critical currents for single specimens.

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[64] That a supercurrent is very well described by regarding all paired electrons as occupying a single quantum state is confirmed by the absence of thermoelectric effects in a superconductor (see page 730). If a supercurrent resembled the disorderly flow of electrons that constitutes a current in a normal metal, then there would be an accompanying thermal current (Peltier effect).

[65] Recall (page 742) that within the radius of a given pair will be found the centers of millions of other pairs.

[66] Thus, in principle, supercurrent-carrying states are only metastable. For suitable geometries (i.e., specimens that are very small in one spatial dimension or more) the fluctuations necessary to destroy a supercurrent need not be overwhelmingly improbable, and one can observe the decay of the "persistent current." A very appealing microscopic picture of such processes has been given by V. Ambegaokar and J. S. Langer, *Phys. Rev.* 164, 498 (1967).

[67] B. D. Josephson, *Phys. Lett.* 1, 251 (1962). See also the articles by Josephson and Mercereau in *Superconductivity*, R. D. Parks, ed., Dekker, New York, 1969.

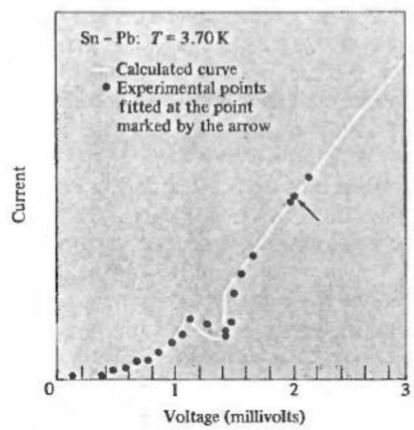

Figure 34.10
Normal tunneling current between two superconductors (tin and lead). The solid curve is the prediction of BCS theory. (S. Shapiro et al., *IBM J. Res. Develop.* 6, 34 (1962).)

Josephson predicted a variety of further effects by assuming that the superconducting ordering on both sides of the junction could be described by a single order parameter $\psi(\mathbf{r})$. He showed that the tunneling current would be determined by the change in phase of the order parameter across the junction. Furthermore, by using gauge invariance to relate the phase of the order parameter to the value of an applied vector potential, he was able to show that the tunneling current would depend in a sensitive way upon any magnetic field present in the junction. Specifically, the tunneling current in the presence of a magnetic field should have the form

$$I = I_0 \frac{\sin \pi\Phi/\Phi_0}{\pi\Phi/\Phi_0}, \tag{34.35}$$

where Φ is the total magnetic flux in the junction, Φ_0 is the flux quantum $hc/2e$, and I_0 depends on the temperature and the structure of the junction, but not upon magnetic field. Such effects were subsequently observed (Figure 34.11), thereby providing impressive further confirmation of the fundamental validity of the order parameter description of the superconducting state, as well as vindicating Josephson's highly imaginative application of the theory.[68]

Similar considerations led Josephson to predict further that if a DC electric potential were applied across such a junction the induced supercurrent would be oscillatory (the AC Josephson effect) with angular frequency

$$\omega_J = \frac{2eV}{\hbar}. \tag{34.36}$$

This remarkable result—that a DC electric field should induce an alternating current—was not only observed, but has been made the basis for highly accurate techniques for measuring voltages as well as the precise value of the fundamental constant e/h.[69]

[68] The value of the flux quantum is exceedingly small, making the effect of practical importance as an highly sensitive way to measure magnetic field strengths.

[69] W. H. Parker et al., *Phys. Rev.* 177, 639 (1969).

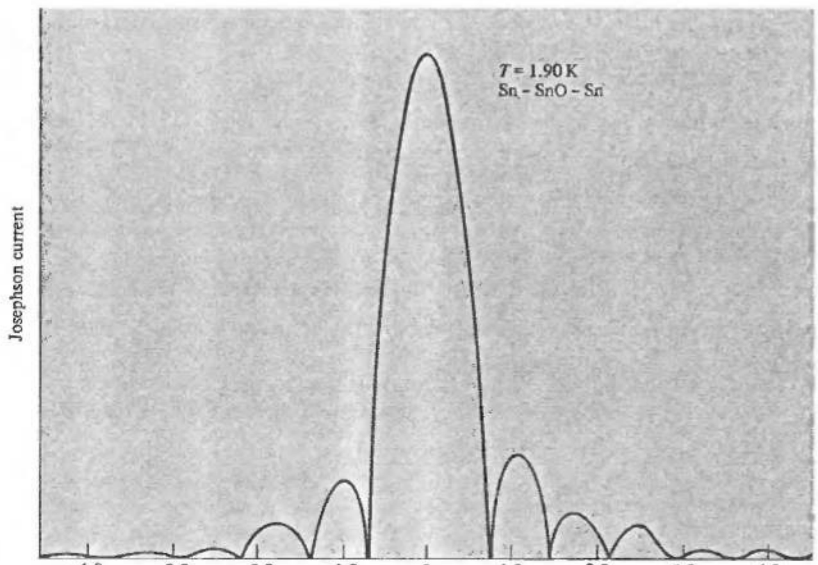

Figure 34.11
Josephson tunneling current as a function of magnetic field in an Sn-SnO-Sn junction. (R. C. Jaklevic, quoted in James E. Mercereau, *Superconductivity*, vol. 1, R. D. Parks, ed., Dekker, New York, 1969, p. 393.)

It is fitting that this volume should conclude with this sketchy and tantalizingly incomplete survey of superconductivity. The rich and highly original theories, both microscopic and phenomenological, that have successfully evolved over the past two decades to cope with superconducting phenomena are indicative of the fundamental health and future promise of the contemporary theory of solids. In spite of the novelty and, at times, the forbidding complexity of the concepts upon which the theory of superconductivity is based, one must not forget that it rests on a broad foundation extending over almost all the important areas of the theory of solids we have examined in earlier chapters. In no other subject are the two fundamental branches of solid state physics—the dynamics of electrons and the vibrations of the lattice of ions—so intimately fused, with such spectacular consequences.

PROBLEMS

1. *Thermodynamics of the Superconducting State*

The equilibrium state of a superconductor in a uniform magnetic field is determined by the temperature T and the magnitude of the field H. (Assume that the pressure P is fixed, and that the superconductor is a long cylinder parallel to the field so that demagnetization effects are unimportant.) The thermodynamic identity is conveniently written in terms of the Gibbs free energy G:

$$dG = -S\,dT - \mathcal{M}\,dH \tag{34.37}$$

where S is the entropy and $\mathcal{M}$, the total magnetization ($\mathcal{M} = MV$, where M is the magnetization density). The phase boundary between the superconducting and normal states in the H-T plane is given by the critical field curve, $H_c(T)$ (Figure 34.3).

(a) Deduce, from the fact that G is continuous across the phase boundary, that

$$\frac{dH_c(T)}{dT} = \frac{S_n - S_s}{\mathcal{M}_s - \mathcal{M}_n}, \tag{34.38}$$

(where the subscripts s and n indicate values in the superconducting and normal phase, respectively).

(b) Using the fact that the superconducting state displays perfect diamagnetism ($B = 0$), while the normal state has negligible diamagnetism ($M \approx 0$), show from (34.38) that the entropy discontinuity across the phase boundary is

$$S_n - S_s = -\frac{V}{4\pi} H_c \frac{dH_c}{dT}, \tag{34.39}$$

and thus the latent heat, when the transition occurs in a field, is

$$Q = -TV \frac{H_c}{4\pi} \frac{dH_c}{dT}. \tag{34.40}$$

(c) Show that when the transition occurs at zero field (i.e., at the critical point) there is a specific heat discontinuity given by

$$(c_p)_n - (c_p)_s = -\frac{T}{4\pi}\left(\frac{dH_c}{dT}\right)^2. \tag{34.41}$$

2. *The London Equation for a Superconducting Slab*

Consider an infinite superconducting slab bounded by two parallel planes perpendicular to the y-axis at $y = \pm d$. Let a uniform magnetic field of strength H_0 be applied along the z-axis.

(a) Taking as a boundary condition that the parallel component of $\mathbf{B}$ be continuous at the surface, deduce from the London equation (34.7) and the Maxwell equation (34.6) that within the superconductor

$$\mathbf{B} = B(y)\hat{\mathbf{z}}, \quad B(y) = H_0 \frac{\cosh(y/\Lambda)}{\cosh(d/\Lambda)}. \tag{34.42}$$

(b) Show that the diamagnetic current density flowing in equilibrium is

$$\mathbf{j} = j(y)\hat{\mathbf{x}}, \quad j(y) = \frac{c}{4\pi\Lambda} H_0 \frac{\sinh(y/\Lambda)}{\cosh(d/\Lambda)}.$$

(c) The magnetization density at a point within the slab is $\mathbf{M}(y) = (\mathbf{B}(y) - \mathbf{H}_0)/4\pi$. Show that the average magnetization density (averaged over the thickness of the slab) is

$$\overline{M} = -\frac{H_0}{4\pi}\left(1 - \frac{\Lambda}{d}\tanh\frac{d}{\Lambda}\right), \tag{34.43}$$

and give the limiting form for the susceptibility when the slab is thick ($d \gg \Lambda$) and thin ($d \ll \Lambda$).

3. *Critical Current in a Cylindrical Wire*

A current of I amperes flows in a cylindrical superconducting wire of radius r cm. Show that when the field produced by the current immediately outside the wire is H_c (in gauss), then

$$I = 5rH_c. \tag{34.44}$$

4. *The Cooper Problem*

Consider a pair of electrons in a singlet state, described by the symmetric spatial wave function

$$\phi(\mathbf{r} - \mathbf{r}') = \int \frac{d\mathbf{k}}{(2\pi)^3}\, \chi(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \tag{34.45}$$

In the momentum representation the Schrödinger equation has the form

$$\left(E - 2\frac{\hbar^2 k^2}{2m}\right)\chi(\mathbf{k}) = \int \frac{d\mathbf{k}'}{(2\pi)^3}\, V(\mathbf{k}, \mathbf{k}')\chi(\mathbf{k}'). \tag{34.46}$$

We assume that the two electrons interact in the presence of a degenerate free electron gas, whose existence is felt only via the exclusion principle: Electron levels with $k < k_F$ are forbidden to each of the two electrons, which gives the constraint:

$$\chi(\mathbf{k}) = 0, \quad k < k_F. \tag{34.47}$$

We take the interaction of the pair to have the simple attractive form (cf. Eq. (34.16)):

$$\begin{aligned} V(\mathbf{k}_1\, \mathbf{k}_2) &\equiv -V, \qquad \mathcal{E}_F \leqslant \frac{\hbar^2 k_i^{\,2}}{2m} \leqslant \mathcal{E}_F + \hbar\omega, \quad i = 1, 2; \\ &= 0, \qquad \text{otherwise}, \end{aligned} \tag{34.48}$$

and look for a bound-state solution to the Schrödinger equation (34.46) consistent with the constraint (34.47). Since we are considering only one-electron levels which in the absence of the attraction have energies in excess of $2\mathcal{E}_F$, a bound state will be one with energy E less than $2\mathcal{E}_F$, and the binding energy will be

$$\Delta = 2\mathcal{E}_F - E. \tag{34.49}$$

(a) Show that a bound state of energy E exists provided that

$$1 = V \int_{\mathcal{E}_F}^{\mathcal{E}_F + \hbar\omega} \frac{N(\mathcal{E})\, d\mathcal{E}}{2\mathcal{E} - E}, \tag{34.50}$$

where $N(\mathcal{E})$ is the density of one-electron levels of a given spin.

(b) Show that Eq. (34.50) has a solution with $E < 2\mathcal{E}_F$ for arbitrarily weak V, provided that $N(\mathcal{E}_F) \neq 0$. (Note the crucial role played by the exclusion principle: If the lower cutoff were not $\mathcal{E}_F$, but 0, then since $N(0) = 0$, there would *not* be a solution for arbitrarily weak coupling).

(c) Assuming that $N(\mathcal{E})$ differs negligibly from $N(\mathcal{E}_F)$ in the range $\mathcal{E}_F < \mathcal{E} < \mathcal{E}_F + \hbar\omega$, show that the binding energy is given by

$$\Delta = 2\hbar\omega \frac{e^{-2/N(\mathcal{E}_F)V}}{1 - e^{-2/N(\mathcal{E}_F)V}}, \tag{34.51}$$

or, in the weak-coupling limit:

$$\Delta = 2\hbar\omega e^{-2/N(\mathcal{E}_F)V}. \tag{34.52}$$