CHAPTER 12: SUPERCONDUCTIVITY

The electrical resistivity of many metals and alloys drops suddenly to zero when the specimen is cooled to a sufficiently low temperature, often a temperature in the liquid helium range. This phenomenon, called superconductivity, was observed first by Kamerlingh Onnes in Leiden in 1911, three years after he first liquefied helium. At a critical temperature $T_c$, the specimen undergoes a phase transition from a state of normal electrical resistivity to a superconducting state, Fig. 1.

Superconductivity is now very well understood. It is a field with many practical and theoretical aspects. The length of this chapter and the relevant appendices reflect the richness and subtleties of the field.

EXPERIMENTAL SURVEY

In the superconducting state the dc electrical resistivity is zero, or so close to zero that persistent electrical currents have been observed to flow without attenuation in superconducting rings for more than a year, until at last the experimentalist wearied of the experiment.

The decay of supercurrents in a solenoid was studied by File and Mills using precision nuclear magnetic resonance methods to measure the magnetic field associated with the supercurrent. They concluded that the decay time of the supercurrent is not less than 100,000 years. We estimate the decay time below.

In some superconducting materials, particularly those used for superconducting magnets, finite decay times are observed because of an irreversible redistribution of magnetic flux in the material.

The magnetic properties exhibited by superconductors are as dramatic as their electrical properties. The magnetic properties cannot be accounted for by the assumption that a superconductor is a normal conductor with zero electrical resistivity.

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1 H. Kamerlingh Onnes, Akad. van Wetenschappen (Amsterdam) 14, 113, 818 (1911): "The value of the mercury resistance used was 172.7 ohms in the liquid condition at 0°C, extrapolation from the melting point to 0°C by means of the temperature coefficient of solid mercury gives a resistance corresponding to this of 39.7 ohms in the solid state. At 4.3 K this had sunk to 0.084 ohms, that is, to 0.0021 times the resistance which the solid mercury would have at 0°C. At 3 K the resistance was found to have fallen below $3 \times 10^{-6}$ ohms, that is to one ten-millionth of the value which it would have at 0°C. As the temperature sank further to 1.5 K this value remained the upper limit of the resistance." Historical references are given by C. J. Gorter, Rev. Mod. Phys. 36, 1 (1964).

Will every nonmagnetic metallic element become a superconductor at sufficiently low temperatures? We do not know. In experimental searches for superconductors with ultralow transition temperatures it is important to eliminate from the specimen even trace quantities of foreign paramagnetic elements, because they can lower the transition temperature severely. One part of Fe in $10^4$ will destroy the superconductivity of Mo, which when pure has $T_c = 0.92$ K, and 1 at. percent of gadolinium lowers the transition temperature of lanthanum from 5.6 K to 0.6 K. Nonmagnetic impurities have no very marked effect on the transition temperature. The transition temperatures of a number of interesting superconducting compounds are listed in Table 2. Several organic compounds show superconductivity at fairly low temperatures.

**Destruction of Superconductivity by Magnetic Fields**

A sufficiently strong magnetic field will destroy superconductivity. The threshold or critical value of the applied magnetic field for the destruction of superconductivity is denoted by $H_c(T_c)$ and is a function of the temperature. At the critical temperature the critical field is zero: $H_c(T_c) = 0$. The variation of the critical field with temperature for several superconducting elements is shown in Fig. 3.

The threshold curves separate the superconducting state in the lower left of the figure from the normal state in the upper right. Note: We should denote the critical value of the applied magnetic field as $B_{ac}$, but this is not common practice among workers in superconductivity. In the CGS system we shall always understand that $H_c = B_{ac}$, and in the SI we have $H_c = B_{ac}/\mu_0$. The symbol $B_a$ denotes the applied magnetic field.

**Meissner Effect**

Meissner and Oehsenfeld (1933) found that if a superconductor is cooled in a magnetic field to below the transition temperature, then at the transition the lines of induction $B$ are pushed out (Fig. 2). The Meissner effect shows that a bulk superconductor behaves as if inside the specimen $B = 0$.

**Table 2** Superconductivity of selected compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$, in K</th>
<th>Compound</th>
<th>$T_c$, in K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₃Sn</td>
<td>18.05</td>
<td>V₃Ga</td>
<td>16.5</td>
</tr>
<tr>
<td>Nb₃Ge</td>
<td>23.2</td>
<td>V₃Si</td>
<td>17.1</td>
</tr>
<tr>
<td>Nb₂Al</td>
<td>17.5</td>
<td>Pb₂Mo₅S₁₆</td>
<td>14.4</td>
</tr>
<tr>
<td>NbN</td>
<td>16.0</td>
<td>Ti₃Co</td>
<td>3.44</td>
</tr>
<tr>
<td>(SN)₉ polymer</td>
<td>0.26</td>
<td>La₃In</td>
<td>10.4</td>
</tr>
</tbody>
</table>

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Now consider a normal nonmagnetic metal. If we neglect the small susceptibility of a metal in the normal state, then \( M = 0 \) and the energy of the normal metal is independent of field. At the critical field we have

\[
F_N(B_{ac}) = F_N(0) .
\] (7)

The results (6) and (7) are all we need to determine the stabilization energy of the superconducting state at absolute zero. At the critical value \( B_{ac} \) of the applied magnetic field the energies are equal in the normal and superconducting states:

\[
F_N(B_{ac}) = F_S(B_{ac}) = F_S(0) + B_{ac}^2/8\pi ,
\] (8)

\[
F_N(B_{ac}) = F_S(B_{ac}) = F_S(0) + B_{ac}^2/2\mu_0 .
\] (SI)

In SI units \( H_c = B_{ac}/\mu_0 \), whereas in CGS units \( H_c = B_{ac} \).

The specimen is stable in either state when the applied field is equal to the critical field. Now by (7) it follows that

\[
\Delta F = F_N(0) - F_S(0) = B_{ac}^2/8\pi ,
\] (9)

where \( \Delta F \) is the stabilization free energy density of the superconducting state. For aluminum, \( B_{ac} \) at absolute zero is 105 gauss, so that at absolute zero \( \Delta F = (105)^2/8\pi = 439 \text{ erg cm}^{-3} \), in excellent agreement with the result of thermal measurements, 430 erg cm\(^{-3} \).

At a finite temperature the normal and superconducting phases are in equilibrium when the magnetic field is such that their free energies \( F = U - TS \) are equal. The free energies of the two phases are sketched in Fig. 12 as a function of the magnetic field. Experimental curves of the free energies of the two phases for aluminum are shown in Fig. 7. Because the slopes \( dF/dT \) are equal at the transition temperature, there is no latent heat at \( T_c \).

**London Equation**

We saw that the Meissner effect implies a magnetic susceptibility \( \chi = -1/4\pi \) in CGS in the superconducting state or, in SI, \( \chi = -1 \). This sweeping assumption tends to cut off further discussion, and it does not account for the flux penetration observed in thin films. Can we modify a constitutive equation of electrodynamics (such as Ohm’s law) in some way to obtain the Meissner

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4 Diamagnetism, the magnetization \( M \), and the magnetic susceptibility are defined in Chapter 14. The magnitude of the apparent diamagnetic susceptibility of bulk superconductors is very much larger than in typical diamagnetic substances. In (1), \( M \) is the magnetization equivalent to the superconducting currents in the specimen.

Figure 12 The free energy density $F_N$ of a nonmagnetic normal metal is approximately independent of the intensity of the applied magnetic field $B_a$. At a temperature $T < T_c$ the metal is a superconductor in zero magnetic field, so that $F_N(T, 0)$ is lower than $F_S(T, 0)$. An applied magnetic field increases $F_S$, by $B_N^2/8\pi$, in CGS units, so that $F_S(T, B_a) = F_S(T, 0) + B^2_N/8\pi$. If $B_a$ is larger than the critical field $B_{cr}$ the free energy density is lower in the normal state than in the superconducting state, and now the normal state is the stable state. The origin of the vertical scale in the drawing is at $F_S(T, 0)$. The figure equally applies to $U_S$ and $U_N$ at $T = 0$.

Figure 13 Penetration of an applied magnetic field into a semi-infinite superconductor. The penetration depth $\lambda$ is defined as the distance in which the field decreases by the factor $e^{-1}$. Typically, $\lambda \approx 500$ Å in a pure superconductor.

The free energy density $F_N$ of a nonmagnetic normal metal is approximately independent of the intensity of the applied magnetic field $B_a$. At a temperature $T < T_c$ the metal is a superconductor in zero magnetic field, so that $F_N(T, 0)$ is lower than $F_S(T, 0)$. An applied magnetic field increases $F_S$, by $B_N^2/8\pi$, in CGS units, so that $F_S(T, B_a) = F_S(T, 0) + B^2_N/8\pi$. If $B_a$ is larger than the critical field $B_{cr}$ the free energy density is lower in the normal state than in the superconducting state, and now the normal state is the stable state. The origin of the vertical scale in the drawing is at $F_S(T, 0)$. The figure equally applies to $U_S$ and $U_N$ at $T = 0$.

We do not want to modify the Maxwell equations themselves. Electrical conduction in the normal state of a metal is described by Ohm's law $j = \sigma E$. We need to modify this drastically to describe conduction and the Meissner effect in the superconducting state. Let us make a postulate and see what happens.

We postulate that in the superconducting state the current density is directly proportional to the vector potential $A$ of the local magnetic field, where $B = \text{curl} A$. The gauge of $A$ will be specified. In CGS units we write the constant of proportionality as $-c/4\pi\lambda^2_L$, for reasons that will become clear. Here $c$ is the speed of light and $\lambda_L$ is a constant with the dimensions of length. In SI units we write $-1/\mu_0\lambda^2_L$. Thus

\[
\begin{align*}
\text{(CGS)} & \quad j = \frac{c}{4\pi\lambda^2_L} A ; \\
\text{(SI)} & \quad j = \frac{1}{\mu_0\lambda^2_L} A .
\end{align*}
\]

This is the London equation. We express it another way by taking the curl of both sides to obtain

\[
\begin{align*}
\text{(CGS)} & \quad \text{curl} j = -\frac{c}{4\pi\lambda^2_L} B ; \\
\text{(SI)} & \quad \text{curl} j = -\frac{1}{\mu_0\lambda^2_L} B .
\end{align*}
\]

The London equation (10) is understood to be written with the vector potential in the London gauge in which div $A = 0$, and $A_n = 0$ on any external surface through which no external current is fed. The subscript $n$ denotes the component normal to the surface. Thus div $j = 0$ and $j_n = 0$, the actual physical boundary conditions. The form (10) applies to a simply connected superconductor; additional terms may be present in a ring or cylinder, but (11) holds true independent of geometry.

First we show that the London equation leads to the Meissner effect. By a Maxwell equation we know that

\[
\begin{align*}
\text{(CGS)} & \quad \text{curl} B = \frac{4\pi}{c} j ; \\
\text{(SI)} & \quad \text{curl} B = \mu_0 j .
\end{align*}
\]

under static conditions. We take the curl of both sides to obtain

\[
\begin{align*}
\text{(CGS)} & \quad \text{curl} \text{curl} B = -\nabla^2 B = \frac{4\pi}{c} \text{curl} j ; \\
\text{(SI)} & \quad \text{curl} \text{curl} B = -\nabla^2 B = \mu_0 \text{curl} j ,
\end{align*}
\]

which may be combined with the London equation (11) to give for a superconductor

\[
\nabla^2 B = B/\lambda^2_L .
\]

This equation is seen to account for the Meissner effect because it does not allow a solution uniform in space, so that a uniform magnetic field cannot exist in a superconductor. That is, $B(r) \equiv B_0$ is constant is not a solution of (13) unless the constant field $B_0$ is identically zero. The result follows because $\nabla^2 B_0$ is always zero, but $B_0/\lambda^2_L$ is not zero unless $B_0$ is zero. Note further that (12) ensures that $j = 0$ in a region where $B = 0$.

In the pure superconducting state the only field allowed is exponentially damped as we go in from an external surface. Let a semi-infinite superconductor occupy the space on the positive side of the $x$ axis, as in Fig. 13. If $B(0)$ is the field at the plane boundary, then the field inside is

\[
B(x) = B(0) \exp(-x/\lambda_L) ,
\]

(14)