

CHAPTER
3

THE BCS
THEORY

Although this book emphasizes the phenomenological rather than the microscopic theory of superconductivity, it seems appropriate to put “basic BCS” early in the treatment because this theory¹ revolutionized the quality of our understanding of superconductivity. It deepens our understanding of the phenomenological theory by providing the framework for *calculating* the parameters of that theory, such as H_c and λ , as well as showing how to treat phenomena which require a more microscopic approach, such as the energy gap and coherence factors.

Unfortunately, putting this survey of the BCS theory so early in the book has a pedagogical disadvantage: It is one of the more forbidding chapters, largely because the technique of second quantization is used. To minimize this problem, we have kept the treatment as simple as possible and give some explanation of the method to assist a novice to follow the presentation. It is also worth emphasizing that the phenomenological theory, to which the rest of the book is largely devoted, was generally developed to explain experimental observations independently of, and prior to, its “deduction” from microscopic theory. The phenomenological theory can be studied, appreciated, and used in practice with only a limited “cultural” understanding of the microscopic theory. Thus, readers are urged not to allow themselves to get bogged down in this chapter. If this threatens, skim quickly ahead to Sec. 3.11 on the theory of the penetration depth and

¹J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

the concluding summary. Then in reading later chapters, simply refer back to this chapter when necessary to clarify specific points.

3.1 COOPER PAIRS

The basic idea that even a weak attraction can bind pairs of electrons into a bound state was presented by Cooper² in 1956. He showed that the Fermi sea of electrons is unstable against the formation of at least one bound pair, regardless of how weak the interaction is, so long as it is attractive. This result is a consequence of the Fermi statistics and of the existence of the Fermi-sea background, since it is well known that binding does not ordinarily occur in the two-body problem in three dimensions until the strength of the potential exceeds a finite threshold value.

To see how this binding comes about, we consider a simple model of two electrons added to a Fermi sea at $T = 0$, with the stipulation that the extra electrons interact with each other but not with those in the sea, except via the exclusion principle. Thus, we seek a two-particle wavefunction. By the general arguments of Bloch, we expect the lowest-energy state to have zero total momentum, so that the two electrons must have equal and opposite momenta. This suggests building up an orbital wavefunction of the sort

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{k}} g_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-i\mathbf{k}\cdot\mathbf{r}_2}$$

Taking into account the antisymmetry of the total wavefunction with respect to exchange of the two electrons, ψ_0 is converted either to a sum of products of $\cos \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)$ with the antisymmetric singlet spin function $(\alpha_1\beta_2 - \beta_1\alpha_2)$ or to a sum of products of $\sin \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)$ with one of the symmetric triplet spin functions $(\alpha_1\alpha_2, \alpha_1\beta_2 + \beta_1\alpha_2, \beta_1\beta_2)$. (In these expressions, α_1 refers to the “up” spin state of particle 1, whereas β_1 refers to its “down” state.) Anticipating an attractive interaction, we expect the singlet coupling to have lower energy because the cosinoidal dependence of its orbital wavefunction on $(\mathbf{r}_1 - \mathbf{r}_2)$ gives a larger probability amplitude for the electrons to be near each other. Thus, we consider a two-electron singlet wavefunction of the form

$$\psi_0(\mathbf{r}_1 - \mathbf{r}_2) = \left[\sum_{k > k_F} g_{\mathbf{k}} \cos \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) \right] (\alpha_1\beta_2 - \beta_1\alpha_2) \quad (3.1)$$

By inserting (3.1) into the Schrödinger equation of the problem, one can show that the weighting coefficients $g_{\mathbf{k}}$ and the energy eigenvalue E are to be determined by solving

$$(E - 2\epsilon_{\mathbf{k}})g_{\mathbf{k}} = \sum_{k' > k_F} V_{\mathbf{k}\mathbf{k}'} g_{\mathbf{k}'} \quad (3.2)$$

²L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).

In this expression, the $\epsilon_{\mathbf{k}}$ are unperturbed plane-wave energies, and the $V_{\mathbf{k}\mathbf{k}'}$ are the matrix elements of the interaction potential

$$V_{\mathbf{k}\mathbf{k}'} = \Omega^{-1} \int V(\mathbf{r}) e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d\mathbf{r} \quad (3.3)$$

where \mathbf{r} is the distance between the two electrons and Ω is the normalization volume. This $V_{\mathbf{k}\mathbf{k}'}$ characterizes the strength of the potential for scattering a pair of electrons with momenta $(\mathbf{k}', -\mathbf{k}')$ to momenta $(\mathbf{k}, -\mathbf{k})$. If a set of $g_{\mathbf{k}}$ satisfying (3.2) with $E < 2E_F$ can be found, then a bound-pair state exists.

Since it is hard to analyze this situation for general $V_{\mathbf{k}\mathbf{k}'}$, Cooper introduced the very serviceable approximation that all $V_{\mathbf{k}\mathbf{k}'} = -V$ for \mathbf{k} states out to a cutoff energy $\hbar\omega_c$ away from E_F , and that $V_{\mathbf{k}\mathbf{k}'} = 0$ beyond $\hbar\omega_c$. Then the right-hand side of (3.2) is a constant, independent of \mathbf{k} , and we have

$$g_{\mathbf{k}} = V \frac{\sum g_{\mathbf{k}'}}{2\epsilon_{\mathbf{k}} - E} \quad (3.4)$$

Summing both sides and canceling $\sum g_{\mathbf{k}}$, we obtain

$$\frac{1}{V} = \sum_{k > k_F} (2\epsilon_{\mathbf{k}} - E)^{-1} \quad (3.5)$$

When we replace the summation by an integration, with $N(0)$ denoting the density of states at the Fermi level for electrons of one spin orientation, this becomes

$$\frac{1}{V} = N(0) \int_{E_F}^{E_F + \hbar\omega_c} \frac{d\epsilon}{2\epsilon - E} = \frac{1}{2} N(0) \ln \frac{2E_F - E + 2\hbar\omega_c}{2E_F - E}$$

In most classic superconductors, it is found that $N(0)V < 0.3$. This allows use of the so-called *weak-coupling approximation*, valid for $N(0)V \ll 1$, in which the solution to the preceding equation can be written as

$$E \approx 2E_F - 2\hbar\omega_c e^{-2/N(0)V} \quad (3.6)$$

Thus, indeed, there is a bound state with negative energy with respect to the Fermi surface made up entirely of electrons with $k > k_F$, i.e., with kinetic energy in excess of E_F . The contribution to the energy of the attractive potential outweighs this excess kinetic energy, leading to binding regardless of how small V is. Note that the form of the binding energy is not analytic at $V = 0$; i.e., it cannot be expanded in powers of V . As a result, it cannot be obtained by perturbation theory, a fact that greatly delayed the genesis of the theory.

Returning to the wavefunction, we see that the dependence on the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is proportional to

$$\sum_{k > k_F} \frac{\cos \mathbf{k} \cdot \mathbf{r}}{2\xi_{\mathbf{k}} + E'}$$

where we have gone over to energies measured from the Fermi energy, so that

$$\xi_{\mathbf{k}} = \epsilon_{\mathbf{k}} - E_F \quad \text{and} \quad E' = 2E_F - E > 0 \quad (3.7)$$

(Because of the sign change, E' is now the *binding* energy relative to $2E_F$.) Since $g_{\mathbf{k}}$ depends only on $\xi_{\mathbf{k}}$, this solution has spherical symmetry; hence, it is an S state as well as a singlet spin state. Note that the weighting factor $(2\xi_{\mathbf{k}} + E')^{-1}$ has its maximum value $1/E'$ when $\xi_{\mathbf{k}} = 0$, i.e., for electrons *at* the Fermi level, and that it falls off with higher values of $\xi_{\mathbf{k}}$. Thus, the electron states within a range of energy $\sim E'$ above E_F are those most strongly involved in forming the bound state. Since $E' \ll \hbar\omega_c$ for $N(0)V < 1$, this shows that the detailed behavior of $V_{\mathbf{k}\mathbf{k}'}$ out around $\hbar\omega_c$ will not have any great effect on the result. This fact gives us some justification for making such a crude approximation to $V_{\mathbf{k}\mathbf{k}'}$. A second consequence of this small range of energy states is that, by the uncertainty-principle argument of Pippard cited earlier, it implies that the size of the bound pair is not less than $\sim \hbar v_F/E'$. Since kT_c turns out to be of the order of E' , this implies that the size of the Cooper pair state is $\sim \xi_0 = \hbar v_F/kT_c$, much larger than the interparticle distance. Thus, the pairs are highly overlapping.

3.2 ORIGIN OF THE ATTRACTIVE INTERACTION

We now must examine the origin of the negative $V_{\mathbf{k}\mathbf{k}'}$ needed for superconductivity. If we take the bare Coulomb interaction $V(\mathbf{r}) = e^2/r$ and carry out the computation of $V(\mathbf{q})$

$$V(\mathbf{q}) = V(\mathbf{k} - \mathbf{k}') = V_{\mathbf{k}\mathbf{k}'} = \Omega^{-1} \int V(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

we find

$$V(\mathbf{q}) = \frac{4\pi e^2}{\Omega q^2} = \frac{4\pi e^2}{q^2} \quad (3.8)$$

where the last equality holds for unit normalization volume Ω . Evidently, this $V(\mathbf{q})$ is always positive.

Now, if we take into account the dielectric function $\epsilon(\mathbf{q}, \omega)$ of the medium, $V(\mathbf{q})$ is reduced by a factor $\epsilon^{-1}(\mathbf{q}, \omega)$. The most obvious ingredient in $\epsilon(\mathbf{q}, \omega)$ is the screening effect³ of the conduction electrons. This introduces a screening length $1/k_s \approx 1 \text{ \AA}$. In the Fermi-Thomas approximation ϵ is given by $\epsilon = 1 + k_s^2/q^2$, so that

$$V(\mathbf{q}) = \frac{4\pi e^2}{q^2 + k_s^2} \quad (3.9)$$

Thus, the electronic screening has eliminated the divergence at $\mathbf{q} = 0$, but it still leaves a positive $V_{\mathbf{k}\mathbf{k}'}$. Hence, no superconductivity would result.

³See, e.g., J. M. Ziman, *Principles of the Theory of Solids*, Cambridge University Press, New York (1964), Chap. 5.

Negative terms come in only when one takes the motion of the ion cores into account. The physical idea is that the first electron polarizes the medium by attracting positive ions; these excess positive ions in turn attract the second electron, giving an effective attractive interaction between the electrons. If this attraction is strong enough to override the repulsive screened Coulomb interaction, it gives rise to a net attractive interaction, and superconductivity results. Historically, the importance of the electron-lattice interaction in explaining superconductivity was first suggested by Fröhlich⁴ in 1950. This suggestion was confirmed experimentally by the discovery⁵ of the *isotope effect*, i.e., the proportionality of T_c and H_c to $M^{-1/2}$ for isotopes of the same element.

Since these lattice deformations are resisted by the same stiffness that makes a solid elastic, it is clear that the characteristic vibrational, or phonon, frequencies will play a role. (For the electronically screened Coulomb interaction, the characteristic frequency is the plasma frequency, which is so high that we can assume instantaneous response.) From momentum conservation, we can see that if an electron is scattered from \mathbf{k} to \mathbf{k}' , the relevant phonon must carry the momentum $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, and the characteristic frequency must then be the phonon frequency $\omega_{\mathbf{q}}$. As a result, it is plausible that the phonon contribution to the screening function be proportional to $(\omega^2 - \omega_{\mathbf{q}}^2)^{-1}$. Evidently, this resonance denominator gives a *negative* sign if $\omega < \omega_{\mathbf{q}}$, corresponding to the physical argument above; for higher frequencies, i.e., electron energy differences larger than $\hbar\omega_{\mathbf{q}}$, the interaction becomes repulsive. Thus, the cutoff energy $\hbar\omega_c$ of Cooper's attractive matrix element $-V$ is expected to be of the order of the Debye energy $\hbar\omega_D = k\Theta_D$, which characterizes the cutoff of the phonon spectrum.

Early analyses of the best way to treat the coupled electron-phonon system were given by Fröhlich⁶ and by Bardeen and Pines.⁷ The first attempt to test the theoretical criterion for superconductivity systematically throughout the periodic table was a calculation by Pines.⁸ He used the "jellium" model, in which the solid is approximated by a fluid of electrons and point ions, with complete neglect of crystal structure and Brillouin zone effects as well as of the finite ion-core size. As shown in the book of de Gennes,⁹ e.g., the jellium model in a certain approximation leads to

$$V(\mathbf{q}, \omega) = \frac{4\pi e^2}{q^2 + k_s^2} + \frac{4\pi e^2}{q^2 + k_s^2} \frac{\omega_{\mathbf{q}}^2}{\omega^2 - \omega_{\mathbf{q}}^2} \quad (3.10)$$

⁴H. Fröhlich, *Phys. Rev.* **79**, 845 (1950).

⁵E. Maxwell, *Phys. Rev.* **78**, 477 (1950); C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, *Phys. Rev.* **78**, 487 (1950).

⁶H. Fröhlich, *Proc. Roy. Soc. (London)* **A215**, 291 (1952).

⁷J. Bardeen and D. Pines, *Phys. Rev.* **99**, 1140 (1955).

⁸D. Pines, *Phys. Rev.* **109**, 280 (1958).

⁹P. G. de Gennes, *Superconductivity in Metals and Alloys*, W. A. Benjamin, New York (1966), reprinted by Addison-Wesley, Reading, MA, 1989, p. 102.

The first term is the screened Coulomb repulsion, whereas the second term is the phonon-mediated interaction, which is attractive for $\omega < \omega_q$. Unfortunately, (3.10) is too simplified to be of much use as a criterion for superconductivity since it reduces to zero for $\omega = 0$, and it is always negative for $\omega < \omega_q$ regardless of material parameters. It does, however, illustrate that the phonon-mediated interaction is of the same order of magnitude as the direct one, so that the concept of achieving a net, negative interaction matrix element in this way is not unreasonable. In fact, a rather quantitative account of superconducting properties of many specific superconductors has been given by careful microscopic calculations of the band structure and electron-phonon coupling. This work has been discussed in an extensive review by Carbotte,¹⁰ and experimental tests of the role of phonons are cited below in Sec. 3.8.5.

Although the phonon-mediated attraction is the basis for superconductivity in the classic superconductors, it is important to recognize that the BCS pairing model requires only an attractive interaction giving a matrix element that can be approximated as $-V$ over a range of energies near E_F . Different pairing interactions, involving the exchange of bosons other than phonons, may well be responsible for superconductivity in some of the more exotic organic, heavy fermion, and high-temperature superconductors. In this case, the electron pairing may have p -wave or d -wave character, rather than the s -wave form assumed here; in fact, as will be discussed in Sec. 9.9, there is considerable evidence for d -wave pairing in the high-temperature superconductor YBCO. Nonetheless, the macroscopic phenomenology of the resulting superconducting state is changed only in detail by these differences. Hence, the basic BCS model, treated here, underlies the understanding of all superconductors, even the exotic materials for which significant generalizations are required.

3.3 THE BCS GROUND STATE

Having seen that the Fermi sea is unstable against the formation of a bound Cooper pair when the net interaction is attractive, clearly we must then expect pairs to condense until an equilibrium point is reached. This will occur when the state of the system is so greatly changed from the Fermi sea (because of the large number of bound pairs) that the binding energy for an additional pair has gone to zero. Evidently, it would not be easy to handle such a complicated state unless an ingenious mathematical form could be found. Such a form was provided by the BCS wavefunction.

When we write down wavefunctions for more than two electrons, the manner of handling the antisymmetry used above for a single Cooper pair becomes quite awkward, and it is convenient to replace it by a scheme of $N \times N$ Slater

¹⁰J. P. Carbotte, *Revs. Mod. Phys.* **62**, 1027 (1990).

determinants to specify N -electron antisymmetrized product functions. The Slater determinants in turn are more compactly expressed using the language of second quantization, in which the occupied states (including spin index) are specified by the use of "creation operators" such as $c_{\mathbf{k}\uparrow}^*$, which creates an electron of momentum \mathbf{k} and spin up.¹¹ It is also necessary to introduce annihilation operators $c_{\mathbf{k}\downarrow}$ which empty the corresponding state. In this notation, the singlet wavefunction discussed earlier is written

$$|\psi_0\rangle = \sum_{k>k_F} g_{\mathbf{k}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* |F\rangle \quad (3.11)$$

where $|F\rangle$ represents the Fermi sea with all states filled up to k_F . This form makes it obvious that pairs of time-reversed states are always occupied together, a feature that Anderson¹² showed is maintained in the case of dirty superconductors, where a generalized pairing scheme is needed since \mathbf{k} is no longer a good quantum number. One may verify that (3.11) is equivalent to the form (3.1) given above for singlet pairing by summing the two 2×2 Slater determinants with the (equal) coefficients $g_{\mathbf{k}}$ and $g_{-\mathbf{k}}$.

Since electrons obey Fermi statistics, the creation and annihilation operators introduced earlier obey the characteristic anticommutation relations of fermion operators

$$\begin{aligned} [c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma'}^*]_+ &\equiv c_{\mathbf{k}\sigma} c_{\mathbf{k}'\sigma'}^* + c_{\mathbf{k}'\sigma'}^* c_{\mathbf{k}\sigma} = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma'} \\ [c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma'}]_+ &= [c_{\mathbf{k}\sigma}^*, c_{\mathbf{k}'\sigma'}^*]_+ = 0 \end{aligned} \quad (3.12)$$

where σ refers to the spin index. The particle number operator $n_{\mathbf{k}\sigma}$ is defined by

$$n_{\mathbf{k}\sigma} = c_{\mathbf{k}\sigma}^* c_{\mathbf{k}\sigma} \quad (3.13)$$

which has an eigenvalue of unity when operating on an occupied state and gives zero when operating on an empty state. For our purposes, only elementary manipulations using these rules will be required in carrying out applications of this formalism. We use it simply as a compact notation for dealing with many-electron wavefunctions and operators which act on them.

We approach the BCS wavefunction by observing that the most general N -electron wavefunction expressed in terms of momentum eigenfunctions and with the Cooper pairing built in is

$$|\psi_N\rangle = \sum g(\mathbf{k}_1, \dots, \mathbf{k}_l) c_{\mathbf{k}_1\uparrow}^* c_{-\mathbf{k}_1\downarrow}^* \cdots c_{\mathbf{k}_l\uparrow}^* c_{-\mathbf{k}_l\downarrow}^* |\phi_0\rangle$$

where $|\phi_0\rangle$ is the vacuum state with no particles present, \mathbf{k}_1 and \mathbf{k}_l designate the first and last of the M \mathbf{k} values in the band which are occupied in a given term in the sum, and g specifies the weight with which the product of this set of $N/2$ pairs

¹¹We retain the original notation of BCS, but note that $c_{\mathbf{k}\uparrow}^*$ is written as $c_{\mathbf{k}\uparrow}^\dagger$ in more modern notation.

¹²P. W. Anderson, *J. Phys. Chem. Solids* **11**, 26 (1959).

of creation operators appears. The sum runs over all \mathbf{k} values in the band. Since there are

$$\frac{M!}{[M - (N/2)]!(N/2)!} \approx 10^{(10^{20})}$$

ways of choosing the $N/2$ states for pair occupancy, there will be that many terms in the sum and that many of the $g(\mathbf{k}, \dots)$ to determine. This is obviously hopeless. BCS argued that with so many particles involved it would be a good approximation to use a Hartree self-consistent field or *mean-field* approach, in which the occupancy of each state \mathbf{k} is taken to depend solely on the *average* occupancy of other states. In its simplest form, this relaxes the constraint on the total number of particles being N since occupancies are treated only statistically. However, because the number of particles is huge, no serious error is made by working with a system in which only \bar{N} is fixed. Essentially we work in a grand canonical ensemble.

BCS took as their form for the ground state

$$|\psi_G\rangle = \prod_{\mathbf{k} = \mathbf{k}_1, \dots, \mathbf{k}_M} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*) |\phi_0\rangle \quad (3.14)$$

where $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. This form implies that the probability of the pair $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ being occupied is $|v_{\mathbf{k}}|^2$, whereas the probability that it is unoccupied is $|u_{\mathbf{k}}|^2 = 1 - |v_{\mathbf{k}}|^2$. For simplicity, we can consider $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ all real, but it will soon prove important to let them differ by a phase factor $e^{i\varphi}$, where φ is independent of k , and will turn out to be the phase of the macroscopic condensate wavefunction. Evidently, this $|\psi_G\rangle$ can be expressed as a sum

$$|\psi_G\rangle = \sum_N \lambda_N |\psi_N\rangle \quad (3.15)$$

where each term represents the part of the expansion of the product form (3.14) containing $N/2$ pairs. [These $|\psi_N\rangle$ are special cases of the general form mentioned earlier, in which $g(\mathbf{k}, \dots)$ is given by $\prod_{\mathbf{k}} u_{\mathbf{k}} \prod_{\mathbf{k}'} v_{\mathbf{k}'}$, where \mathbf{k} runs over the $(M - N/2)$ unoccupied pair states and \mathbf{k}' runs over the $N/2$ occupied pair states.] If all the $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are finite, there is a finite probability of any N from 0 to $2M$, and $|\psi_G\rangle$ is not an eigenstate of the number operator. However, the values of $|\lambda_N|^2$ are very sharply peaked about the average value

$$\bar{N} = \sum_{\mathbf{k}} 2|v_{\mathbf{k}}|^2 \quad (3.16)$$

As an illustration of the formal manipulation of these second quantized forms, let us run through the mechanics of how \bar{N} is calculated, although (3.16) is obviously correct in view of the physical significance of $v_{\mathbf{k}}$, mentioned earlier. To start,

$$\begin{aligned}\bar{N} &= \langle N_{op} \rangle = \left\langle \sum_{\mathbf{k}, \sigma} n_{\mathbf{k}\sigma} \right\rangle = \langle \psi_G | \sum_{\mathbf{k}} (c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}\uparrow} + c_{\mathbf{k}\downarrow}^* c_{\mathbf{k}\downarrow}) | \psi_G \rangle \\ &= 2 \sum_{\mathbf{k}} \langle \psi_G | c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}\uparrow} | \psi_G \rangle\end{aligned}$$

since the electrons all occur in pairs with antiparallel spin. Putting in $|\psi_G\rangle$ explicitly yields

$$\begin{aligned}\bar{N} &= 2 \sum_{\mathbf{k}} \langle \phi_0 | (u_{\mathbf{k}}^* + v_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}) c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}\uparrow} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*) \\ &\quad \times \prod_{\mathbf{l} \neq \mathbf{k}} (u_{\mathbf{l}}^* + v_{\mathbf{l}}^* c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow}) (u_{\mathbf{l}} + v_{\mathbf{l}} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^*) | \phi_0 \rangle\end{aligned}$$

In writing this, we have used the property that $\langle A\phi | \psi \rangle = \langle \phi | A^\dagger | \psi \rangle$, and that the adjoint of a product of operators is the product of the adjoints in reverse order. Also, we have been able to rearrange the order of factors in the products to group together all those concerning a given pair state \mathbf{k} or \mathbf{l} because, by (3.12), commutation of even numbers of dissimilar Fermi operators introduces no sign change. As we proceed to evaluate this expression, we may think of $|\phi_0\rangle$ as the product of vacuum states for each \mathbf{k} value. This enables the factor relating to each pair to be evaluated separately. Multiplying out the factor for $\mathbf{l} \neq \mathbf{k}$, we have

$$|u_{\mathbf{l}}|^2 + u_{\mathbf{l}}^* v_{\mathbf{l}} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^* + v_{\mathbf{l}}^* u_{\mathbf{l}} c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} + |v_{\mathbf{l}}|^2 c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^*$$

When we take the $\langle \phi_0 | \cdot | \phi_0 \rangle$ matrix element of this expression, the middle two terms give zero since they change the occupancy of the \mathbf{l} th pair. The last term creates and then annihilates the pair, leading to a factor of unity. [More carefully, using the commutation relations (3.12), the operators in the last term can be transformed by successive binary interchanges to $-c_{\mathbf{l}\uparrow} c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^*$, $+(c_{\mathbf{l}\uparrow} c_{\mathbf{l}\uparrow}^*)(c_{-\mathbf{l}\downarrow} c_{-\mathbf{l}\downarrow}^*)$, and $+(1 - c_{\mathbf{l}\uparrow} c_{\mathbf{l}\uparrow})(1 - c_{-\mathbf{l}\downarrow} c_{-\mathbf{l}\downarrow})$, both factors of which give unity when operating on $|\phi_0\rangle$.] Thus, each factor for $\mathbf{l} \neq \mathbf{k}$ simply reduces to $|u_{\mathbf{l}}|^2 + |v_{\mathbf{l}}|^2 = 1$. When the same procedure is followed in the product with $\mathbf{l} = \mathbf{k}$, the cross terms in $u_{\mathbf{k}} v_{\mathbf{k}}$ still drop out since the extra factor $c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}\uparrow}$ leaves particle conservation unaffected. Moreover, because $c_{\mathbf{k}\uparrow} | \phi_0 \rangle$ gives zero, the $|u_{\mathbf{k}}|^2$ term also drops out, leaving simply $|v_{\mathbf{k}}|^2$. Thus, we recover (3.16) as anticipated.

To estimate the sharpness of the peak at \bar{N} , one needs to evaluate

$$\langle (N - \bar{N})^2 \rangle = \langle N^2 - 2N\bar{N} + \bar{N}^2 \rangle = \langle N^2 \rangle - \bar{N}^2$$

Carrying through a calculation similar to that above, one finds

$$\langle (N - \bar{N})^2 \rangle = 4 \sum_{\mathbf{k}} u_{\mathbf{k}}^2 v_{\mathbf{k}}^2$$

This is nonzero unless the occupancy cuts off discontinuously. In fact, it will turn out that $v_{\mathbf{k}}$ goes from 1 to 0, and $u_{\mathbf{k}}$ goes from 0 to 1 in an energy range of $\sim kT_c$, so that the sum is $\sim (T_c/T_F)\bar{N}$. Also, note that both \bar{N} and $\langle (N - \bar{N})^2 \rangle$ scale in

proportion to the volume if one compares systems of various sizes but the same particle density. (This follows because the number of \mathbf{k} values in a given energy range is proportional to the volume.) Accordingly,

$$\delta N_{\text{rms}} = \langle (N - \bar{N})^2 \rangle^{1/2} \approx (T_c/T_F)^{1/2} \bar{N}^{1/2} \approx 10^9 \quad (3.17a)$$

while the fractional uncertainty is

$$\frac{\delta N_{\text{rms}}}{\bar{N}} \approx \frac{(T_c/T_F)^{1/2}}{\bar{N}^{1/2}} \approx 10^{-13} \quad (3.17b)$$

Thus, as is typical of many-particle statistical situations, as $N \rightarrow \infty$, the absolute fluctuations become large, but the fractional fluctuations approach zero.

Although for macroscopic samples we can usually ignore exact particle-number conservation, it is useful to note that we can project out the N -particle part of the BCS ground state, if necessary, by a method used by P. W. Anderson.¹³ We write $|\psi_G\rangle$, associating an arbitrary phase factor $e^{i\varphi}$ with the creation of each pair, as

$$|\psi_\varphi\rangle = \prod_{\mathbf{k}} (|u_{\mathbf{k}}| + |v_{\mathbf{k}}| e^{i\varphi} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*) |\phi_0\rangle \quad (3.18a)$$

When we carry out the multiplication over \mathbf{k} , it produces many terms, which can be grouped into a sum of the sort described by (3.15). The members of the $|\psi_N\rangle$ term are identified by a common phase factor $e^{iN\varphi/2}$, where $N/2$ is the number of pairs in an N -particle state. (N must be an even number since only pairs are included in the wavefunction.) We can then project out this $|\psi_N\rangle$ by simply multiplying by $e^{-iN\varphi/2}$ and integrating on φ over 2π , since this gives zero except for those terms in the expansion of the product in (3.18a) in which there are precisely $N/2$ factors of $e^{i\varphi}$, each of which is associated with the creation of a pair. That is,

$$|\psi_N\rangle = \int_0^{2\pi} d\varphi e^{-iN\varphi/2} \prod_{\mathbf{k}} (|u_{\mathbf{k}}| + |v_{\mathbf{k}}| e^{i\varphi} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*) |\phi_0\rangle = \int_0^{2\pi} d\varphi e^{-iN\varphi/2} |\psi_\varphi\rangle \quad (3.18b)$$

By integrating over all values of φ , i.e., by making φ completely uncertain, we have enforced a precise specification of the number N . On the other hand, with φ fixed as in (3.18a), we have seen that $\delta N \approx 10^9$. These results illustrate the uncertainty relation

$$\Delta N \Delta\varphi \gtrsim 1 \quad (3.19)$$

The relation between phase and number will be discussed in greater depth in Sec. 7.3, which deals with mesoscopic systems. These effects become crucial when dealing with small particles, where the large Coulomb energy resulting from any excess electrons forces ΔN to be small.

¹³P. W. Anderson, "The Josephson Effect and Quantum Coherence Measurements in Superconductors and Superfluids," in C. J. Gorter (ed.), *Progress in Low Temp. Phys.* vol. 5, Wiley, New York (1967), p. 5.

There is an instructive analogy to (3.19) in the case of electromagnetic radiation. In order to have a semiclassical electric field \mathbf{E} with well-defined phase and amplitude, one must have enough photons (as in a laser), so that one can tolerate a superposition of states with various numbers of photons present.

3.4 VARIATIONAL METHOD

We have studied the structure of ψ_G with some care to bring out some of its interesting features. Now we must actually make it explicit by finding appropriate values for the $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$. Our first approach is a variational calculation, as was used in the original BCS paper. Later we shall discuss another technique which leads to the same conclusions but in somewhat more modern form.

3.4.1 Determination of the Coefficients

We make the calculation by using the so-called *pairing hamiltonian* or *reduced hamiltonian*

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} \quad (3.20)$$

presuming that it includes the terms that are decisive for superconductivity, although it omits many other terms which involve electrons not paired as $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$. Such terms have zero expectation value in the BCS ground-state wavefunction but may be important in other applications. To regulate the mean number of particles \bar{N} , we include a term $-\mu N_{\text{op}}$, where μ is the chemical potential (or Fermi energy) and N_{op} is the particle-number operator. We then minimize the expectation value of the sum by setting

$$\delta \langle \psi_G | \mathcal{H} - \mu N_{\text{op}} | \psi_G \rangle = 0$$

The inclusion of $-\mu N_{\text{op}}$ is mathematically equivalent to taking the zero of kinetic energy to be μ (or E_F). So, more explicitly, we set

$$\delta \left\langle \psi_G \left| \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} n_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} \right| \psi_G \right\rangle = 0$$

where, as before, $\xi_{\mathbf{k}} = \epsilon_{\mathbf{k}} - \mu$ is the single-particle energy relative to the Fermi energy. By the method of calculation used previously to find \bar{N} , we see at once that the first term yields

$$\langle KE - \mu N \rangle = 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} |v_{\mathbf{k}}|^2 \quad (3.21)$$

Similarly, the interaction term gives

$$\langle V \rangle = \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} u_{\mathbf{k}} v_{\mathbf{k}}^* u_{\mathbf{l}}^* v_{\mathbf{l}} \quad (3.22)$$

as can be seen by direct calculation. Alternatively, it can be seen by inspection by noting that the term $V_{\mathbf{k}\mathbf{l}}$ scatters from a state with $(\mathbf{l}\uparrow, -\mathbf{l}\downarrow)$ to one with $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$. This requires the initial state to have the \mathbf{l} pair occupied and the \mathbf{k} pair empty and vice versa for the final state. The probability *amplitude* for such an initial state is $u_{\mathbf{k}}v_{\mathbf{l}}$ and for the final state it is $v_{\mathbf{k}}^*u_{\mathbf{l}}^*$, thus leading to the preceding result. We should note perhaps that $V_{\mathbf{k}\mathbf{l}}$ contributes nothing to the energy in the normal state. This is obvious at $T = 0$ since states are either 100 percent occupied or empty, so that the product of the probabilities of being full and empty is zero. At $T > 0$, the Fermi distribution does not cut off sharply, and so one might think there would be a nonzero contribution. However, in the normal state, the various Slater determinants representing specific electron occupation numbers are superimposed with random relative phase, so that the appropriate products of probability amplitudes (corresponding to $u_{\mathbf{k}}v_{\mathbf{k}}^*u_{\mathbf{l}}^*v_{\mathbf{l}}$ in the ordered BCS state) average to zero. Hence, these scattering terms make no contribution to the average energy in the normal state.

Combining (3.21) and (3.22), and for simplicity taking $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ to be real, we have

$$\langle \psi_G | \mathcal{H} - \mu N_{\text{op}} | \psi_G \rangle = 2 \sum_{\mathbf{k}} \xi_{\mathbf{k}} v_{\mathbf{k}}^2 + \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{l}} v_{\mathbf{l}} \quad (3.23)$$

which is to be minimized subject to the constraint that $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$. This constraint is conveniently imposed by letting

$$u_{\mathbf{k}} = \sin \theta_{\mathbf{k}} \quad \text{and} \quad v_{\mathbf{k}} = \cos \theta_{\mathbf{k}} \quad (3.24)$$

Then, after using elementary trigonometric identities, the right member of (3.23) can be written

$$\sum_{\mathbf{k}} \xi_{\mathbf{k}} (1 + \cos 2\theta_{\mathbf{k}}) + \frac{1}{4} \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} \sin 2\theta_{\mathbf{k}} \sin 2\theta_{\mathbf{l}}$$

whence

$$\frac{\partial}{\partial \theta_{\mathbf{k}}} \langle \psi_G | \mathcal{H} - \mu N_{\text{op}} | \psi_G \rangle = 0 = -2\xi_{\mathbf{k}} \sin 2\theta_{\mathbf{k}} + \sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} \cos 2\theta_{\mathbf{k}} \sin 2\theta_{\mathbf{l}} \quad (3.25)$$

(The extra factor of 2 enters in the second sum because both \mathbf{k} and \mathbf{l} indices run over any given value \mathbf{k}' .) Thus,

$$\tan 2\theta_{\mathbf{k}} = \frac{\sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} \sin 2\theta_{\mathbf{l}}}{2\xi_{\mathbf{k}}} \quad (3.26)$$

Now we *define* the quantities

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} u_{\mathbf{l}} v_{\mathbf{l}} = -\frac{1}{2} \sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} \sin 2\theta_{\mathbf{l}} \quad (3.27)$$

and

$$E_{\mathbf{k}} = (\Delta_{\mathbf{k}}^2 + \xi_{\mathbf{k}}^2)^{1/2} \quad (3.28)$$

This $E_{\mathbf{k}}$ will soon be shown to be the excitation energy of a quasi-particle of momentum $\hbar\mathbf{k}$, while $\Delta_{\mathbf{k}}$ will be essentially independent of \mathbf{k} , and hence is the minimum excitation energy, or energy gap. It will also become the *order parameter* in the phenomenological theory, having a phase factor $e^{i\varphi}$, where φ is the relative phase of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ as in (3.18a).

With these two definitions, (3.26) becomes

$$\tan 2\theta_{\mathbf{k}} = -\frac{\Delta_{\mathbf{k}}}{\xi_{\mathbf{k}}} \quad (3.29a)$$

so that
$$2u_{\mathbf{k}}v_{\mathbf{k}} = \sin 2\theta_{\mathbf{k}} = \frac{\Delta_{\mathbf{k}}}{E_{\mathbf{k}}} \quad (3.29b)$$

and
$$v_{\mathbf{k}}^2 - u_{\mathbf{k}}^2 = \cos 2\theta_{\mathbf{k}} = -\frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \quad (3.29c)$$

The choice of signs for the sine and cosine [only their relative sign is fixed by (3.29a)] gives the occupation number $v_{\mathbf{k}}^2 \rightarrow 0$ as $\xi_{\mathbf{k}} \rightarrow \infty$, as is required for a reasonable solution.

We can now substitute (3.29b) back into (3.27) to evaluate $\Delta_{\mathbf{k}}$, leading to the condition for self-consistency

$$\Delta_{\mathbf{k}} = -\frac{1}{2} \sum_{\mathbf{l}} \frac{\Delta_{\mathbf{l}}}{E_{\mathbf{l}}} V_{\mathbf{kl}} = -\frac{1}{2} \sum_{\mathbf{l}} \frac{\Delta_{\mathbf{l}}}{(\Delta_{\mathbf{l}}^2 + \xi_{\mathbf{l}}^2)^{1/2}} V_{\mathbf{kl}} \quad (3.30)$$

We note first the trivial solution in which $\Delta_{\mathbf{k}} = 0$, so that $v_{\mathbf{k}} = 1$ for $\xi_{\mathbf{k}} < 0$, and $v_{\mathbf{k}} = 0$ for $\xi_{\mathbf{k}} > 0$. The associated $|\psi\rangle$ is just the single Slater determinant with all states up to \mathbf{k}_F occupied, the normal Fermi sea at $T = 0$. But we expect a nontrivial solution with lower energy if $V_{\mathbf{kl}}$ is negative. We retain the model of $V_{\mathbf{kl}}$ used by Cooper and by BCS, namely,

$$V_{\mathbf{kl}} = \begin{cases} -V & \text{if } |\xi_{\mathbf{k}}| \text{ and } |\xi_{\mathbf{l}}| \leq \hbar\omega_c \\ 0 & \text{otherwise} \end{cases} \quad (3.31)$$

with V being a positive constant. (Our theoretical discussion of $V_{\mathbf{kl}}$ actually suggests that the relevant energy is $|\xi_{\mathbf{k}} - \xi_{\mathbf{l}}|$, the energy change of the electron in the scattering process, but to get a simple solution, we need to make the stronger restriction that $|\xi_{\mathbf{k}}|$ and $|\xi_{\mathbf{l}}|$ separately are smaller than $\hbar\omega_c$.) Inserting this $V_{\mathbf{kl}}$ in (3.30), we find that it is satisfied by

$$\Delta_{\mathbf{k}} = \begin{cases} \Delta & \text{for } |\xi_{\mathbf{k}}| < \hbar\omega_c \\ 0 & \text{for } |\xi_{\mathbf{k}}| > \hbar\omega_c \end{cases} \quad (3.32)$$

Since in this model $\Delta_{\mathbf{k}} = \Delta$ is actually independent of \mathbf{k} , we may cancel it from both sides of (3.30), and our condition for self-consistency then reads

$$1 = \frac{V}{2} \sum_{\mathbf{k}} \frac{1}{E_{\mathbf{k}}} \quad (3.33)$$

Upon replacing the summation by an integration from $-\hbar\omega_c$ to $\hbar\omega_c$, and using the symmetry of $\pm\xi$ values, this becomes

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{(\Delta^2 + \xi^2)^{1/2}} = \sinh^{-1} \frac{\hbar\omega_c}{\Delta} \quad (3.33a)$$

Thus
$$\Delta = \frac{\hbar\omega_c}{\sinh [1/N(0)V]} \approx 2\hbar\omega_c e^{-1/N(0)V} \quad (3.34)$$

where the last step is justified in the weak-coupling limit $N(0)V \ll 1$. Since it will turn out that $N(0)V$ is typically $\lesssim 0.3$ the approximate equality in (3.34) is typically good to 1 percent.

Having found Δ , we may simply compute the coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ which specify the optimum BCS wavefunction. A convenient approach is to start with (3.29c) and the normalization condition $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$. In this way, we find that the fractional occupation number $v_{\mathbf{k}}^2$ is given by

$$v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right) = \frac{1}{2} \left[1 - \frac{\xi_{\mathbf{k}}}{(\Delta^2 + \xi_{\mathbf{k}}^2)^{1/2}} \right] \quad (3.35)$$

whereas
$$u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right) = 1 - v_{\mathbf{k}}^2$$

A plot of $v_{\mathbf{k}}^2$ is shown in Fig. 3.1. Note that $v_{\mathbf{k}}^2$ approaches unity well below the Fermi energy and zero well above, rather like the Fermi function that is appropriate to normal metals at finite temperatures. In fact, there is a startling resemblance between $v_{\mathbf{k}}^2$ for the BCS ground state at $T = 0$ and the normal-metal Fermi function at $T = T_c$, also plotted in Fig. 3.1 for comparison purposes. From this comparison we see that, contrary to the early ideas of Fröhlich, Bardeen, and others, the change in the metal on cooling from T_c to $T = 0$ cannot be usefully described in terms of changes in the occupation numbers of one-electron

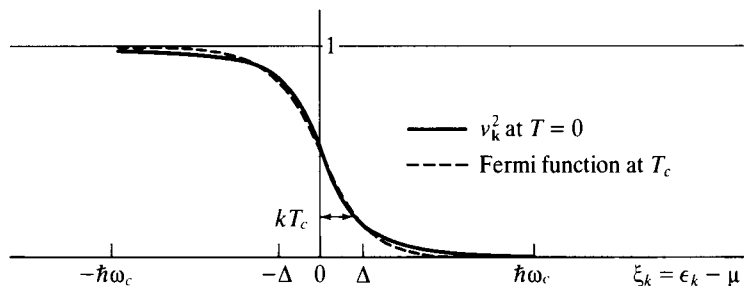


FIGURE 3.1

Plot of BCS occupation fraction $v_{\mathbf{k}}^2 (= 1 - u_{\mathbf{k}}^2)$ vs. electron energy measured from the chemical potential (Fermi energy). To make the cutoffs at $\pm\hbar\omega_c$ visible, the plot has been made for a strong-coupling superconductor with $N(0)V = 0.43$. For comparison, the Fermi function for the normal state at T_c is also shown on the same scale using the BCS relation $\Delta(0) = 1.76kT_c$.

momentum eigenstates. In particular, no gap opens up in \mathbf{k} space. Rather, the disorder associated with partial occupation of these states with *random* phases is being replaced by a *single* quantum state of the system, in which more or less the same set of many-body states with various one-electron occupancies are now superposed with a *fixed* phase relation.

A further remark about our result for $v_{\mathbf{k}}^2$ is that it falls off as $1/\xi_{\mathbf{k}}^2$ for $\xi_{\mathbf{k}} \gg \Delta$, the same dependence as we found earlier for $g_{\mathbf{k}}^2$ in our simple treatment of a single Cooper pair. In fact, apart from the asymmetry introduced by the artificial restriction of keeping the Fermi sea undisturbed, that simple calculation gives quite an accurate idea of how the energy-lowering correlated-pair state is formed. Finally, we note from (3.35) that Δ is the characteristic energy determining the range of \mathbf{k} values involved in forming the Cooper pairs. Since Δ will turn out to be $1.76kT_c$ at $T=0$, this reinforces our expectation of a characteristic size $\sim \xi_0 \sim \hbar v_F/\Delta \sim \hbar v_F/kT_c$.

3.4.2 Evaluation of Ground-State Energy

With $|\psi_G\rangle$ determined, we now calculate its energy, to show that it is indeed lower than the Fermi-sea state. From (3.23), using (3.27) and (3.35), we have

$$\langle \psi_G | \mathcal{H} - \mu N_{\text{op}} | \psi_G \rangle = \sum_{\mathbf{k}} \left(\xi_{\mathbf{k}} - \frac{\xi_{\mathbf{k}}^2}{E_{\mathbf{k}}} \right) - \frac{\Delta^2}{V}$$

As noted earlier, the normal state at $T=0$ corresponds to the BCS state with $\Delta=0$, in which case $E_{\mathbf{k}} = |\xi_{\mathbf{k}}|$. Thus,

$$\langle \psi_n | \mathcal{H} - \mu N_{\text{op}} | \psi_n \rangle = \sum_{|\mathbf{k}| < k_F} 2\xi_{\mathbf{k}}$$

the terms for $|\mathbf{k}| > k_F$ giving zero since $E_{\mathbf{k}} = \xi_{\mathbf{k}}$. Thus, the difference in these energies is

$$\begin{aligned} \langle E \rangle_s - \langle E \rangle_n &= \sum_{|\mathbf{k}| > k_F} \left(\xi_{\mathbf{k}} - \frac{\xi_{\mathbf{k}}^2}{E_{\mathbf{k}}} \right) + \sum_{|\mathbf{k}| < k_F} \left(-\xi_{\mathbf{k}} - \frac{\xi_{\mathbf{k}}^2}{E_{\mathbf{k}}} \right) - \frac{\Delta^2}{V} \\ &= 2 \sum_{|\mathbf{k}| > k_F} \left(\xi_{\mathbf{k}} - \frac{\xi_{\mathbf{k}}^2}{E_{\mathbf{k}}} \right) - \frac{\Delta^2}{V} \end{aligned}$$

by symmetry about the Fermi energy. In this formula, the sum expresses the change in kinetic energy, whereas the term $-\Delta^2/V$ is the change in potential energy. Going over to the continuum approximation, carrying out the integration on ξ from 0 to $\hbar\omega_c$, and using the weak-coupling-limit relation (3.34), we find

$$\langle E \rangle_s - \langle E \rangle_n = \left[\frac{\Delta^2}{V} - \frac{1}{2} N(0) \Delta^2 \right] - \frac{\Delta^2}{V}$$

We have kept the kinetic-energy difference together inside the brackets to make explicit the cancellation of its leading term against the attractive potential-energy

term. Thus, the *net* energy lowering is down by a factor of $N(0)V/2 \approx 0.1$ from the increase in kinetic energy or the decrease in potential energy separately. Introducing the thermodynamic symbol $U(T)$ for the internal energy of the system, and anticipating that $\Delta(T)$ is temperature dependent, we have as our final result

$$U_s(0) - U_n(0) = -\frac{1}{2}N(0)\Delta^2(0) \quad (3.36)$$

This is the *condensation energy* at $T=0$, which must by definition equal $H_c^2(0)/8\pi$, where $H_c(T)$ is the thermodynamic critical field.

3.4.3 Isotope Effect

Since (3.34) shows that Δ is proportional to $\hbar\omega_c$, and since ω_c for different isotopes of the same element should be proportional to $M^{-1/2}$, it follows from (3.36) that the thermodynamic critical field H_c should scale as $M^{-\alpha}$, with $\alpha \approx \frac{1}{2}$. This dependence of H_c (or T_c) on the isotopic mass is called the *isotope effect*. Note that this argument requires the assumption that $N(0)$ and V are unchanged from one isotope to the other. Since $N(0)$ is a purely electronic quantity, it might be expected to be independent of M , but it is less clear for the parameter V , which is determined jointly by the electrons and phonons. In fact, although the isotope-shift exponent α is quite accurately $\frac{1}{2}$ for a few classic superconductors, such as lead, experiments on other materials have shown that it can range all the way to zero or even change sign. Such variations can be accounted for theoretically¹⁴ if one uses a more detailed theory of the interaction than we have been able to give here, but as usual a priori calculations are difficult because they depend on details of the material. It is perhaps more useful to invert the procedure and to try to use the measured isotope effect to gain information about the interaction, as was done for the classic superconductors by McMillan.¹⁵

More recently, the discovery of the high-temperature superconductors has renewed interest in using the isotope effect to try to elucidate the puzzle of the mechanism responsible for the high transition temperature. Since these materials contain several different types of atoms, many different types of isotopic substitution can be studied. One can even differentially substitute a given type of atom on different types of sites in the crystal. These investigations¹⁶ have shown the importance of the phonon spectrum and revealed certain regularities, but no definitive conclusions about mechanisms had been reached at the time of this writing.

¹⁴P. Morel and P. W. Anderson, *Phys. Rev.* **125**, 1263 (1962); J. W. Garland, Jr., *Phys. Rev. Lett.* **11**, 114 (1963)

¹⁵W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).

¹⁶See, e.g., the extensive review by J. P. Franck in D. M. Ginsberg (ed.), *Physical Properties of High Temperature Superconductors IV*, World Scientific, Singapore (1994), pp. 189–293.

3.5 SOLUTION BY CANONICAL TRANSFORMATION

The variational method used in the original BCS treatment, which we have just sketched, is a direct approach for calculating the condensation energy of the superconducting ground state relative to the normal state. It is somewhat clumsy, however, though workable, in dealing with excited states. In this section, we outline another approach, closer to the more sophisticated modern methods, which is well suited to handle excitations. This alternate method is also a self-consistent field method, but no appeal to a variational calculation is required.

We start with the observation that the characteristic BCS pair-interaction hamiltonian will lead to a ground state which is some phase-coherent superposition of many-body states with pairs of Bloch states $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ occupied or unoccupied as units. Because of the coherence, operators such as $c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow}$ can have nonzero expectation values $b_{\mathbf{k}}$ in such a state, rather than averaging to zero as in a normal metal, where the phases are random. Moreover, because of the large numbers of particles involved, the fluctuations about these expectation values should be small. This suggests that it will be useful to express such a product of operators formally as

$$c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} = b_{\mathbf{k}} + (c_{-\mathbf{k}\downarrow}c_{\mathbf{k}\uparrow} - b_{\mathbf{k}}) \quad (3.37)$$

and subsequently neglect quantities which are bilinear in the presumably small fluctuation term in parentheses. If we follow this procedure with our pairing hamiltonian (3.20), we obtain the so-called *model-hamiltonian*

$$\mathcal{H}_M = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^* c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}\mathbf{l}} V_{\mathbf{k}\mathbf{l}} (c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* b_{\mathbf{l}} + b_{\mathbf{k}}^* c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} - b_{\mathbf{k}}^* b_{\mathbf{l}}) \quad (3.38)$$

where the $b_{\mathbf{k}}$ are to be determined self-consistently, so that

$$b_{\mathbf{k}} = \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle_{av} \quad (3.39)$$

Note that in gaining the simplicity of eliminating quartic terms in the $c_{\mathbf{k}}$'s from the hamiltonian, we have thrown it into an approximate form which does not conserve particle number. Rather, there are now terms which create or destroy pairs of particles. This is analogous to the situation noted earlier in which the simple BCS product wavefunction with fixed phase contained many different numbers of particles. Only by integrating over the phase φ were we able to set an exact particle number. The corresponding situation here is that we have assigned a definite phase to $b_{\mathbf{k}}$. In any case, as before, we can handle this situation by introducing the chemical potential μ so as to fix \bar{N} at any desired value.

Now to proceed with the solution, we define

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} b_{\mathbf{l}} = - \sum_{\mathbf{l}} V_{\mathbf{k}\mathbf{l}} \langle c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow} \rangle \quad (3.40)$$

This definition is evidently very analogous to the one given in (3.27), and it will turn out to give the gap in the energy spectrum. In terms of $\Delta_{\mathbf{k}}$, the model hamiltonian becomes (after relabeling some subscripts)

$$\mathcal{H}_M = \sum_{\mathbf{k}\sigma} \xi_{\mathbf{k}} c_{\mathbf{k}\sigma}^* c_{\mathbf{k}\sigma} - \sum_{\mathbf{k}} (\Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* + \Delta_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} - \Delta_{\mathbf{k}} b_{\mathbf{k}}^*) \quad (3.41)$$

which is a sum of terms, each bilinear in the pair of operators corresponding to the partners in a Cooper pair. Such a hamiltonian can be diagonalized by a suitable linear transformation to define new Fermi operators $\gamma_{\mathbf{k}}$. As shown independently by Bogoliubov¹⁷ and by Valatin,¹⁸ the appropriate transformation is specified by

$$\begin{aligned} c_{\mathbf{k}\uparrow} &= u_{\mathbf{k}}^* \gamma_{\mathbf{k}0} + v_{\mathbf{k}} \gamma_{\mathbf{k}1}^* \\ c_{-\mathbf{k}\downarrow}^* &= -v_{\mathbf{k}}^* \gamma_{\mathbf{k}0} + u_{\mathbf{k}} \gamma_{\mathbf{k}1}^* \end{aligned} \quad (3.42)$$

where the numerical coefficients $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ satisfy $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. Note that $\gamma_{\mathbf{k}0}$ participates in destroying an electron with $\mathbf{k}\uparrow$ or creating one with $-\mathbf{k}\downarrow$; in both cases, the net effect is to decrease the system momentum by \mathbf{k} and to reduce S_z by $\hbar/2$. The operator $\gamma_{\mathbf{k}1}^*$ has similar properties, so $\gamma_{\mathbf{k}1}$ itself decreases the system momentum by $-\mathbf{k}$ (i.e., increases it by \mathbf{k}) and has the net effect of increasing S_z .

Substituting these new operators (3.42) into the model hamiltonian (3.41), and carrying out the indicated products taking into account the noncommutivity of the operators, we obtain

$$\begin{aligned} \mathcal{H}_M &= \sum_{\mathbf{k}} \xi_{\mathbf{k}} [(|u_{\mathbf{k}}|^2 - |v_{\mathbf{k}}|^2) (\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0} + \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}1}) + 2|v_{\mathbf{k}}|^2 + 2u_{\mathbf{k}}^* v_{\mathbf{k}}^* \gamma_{\mathbf{k}1} \gamma_{\mathbf{k}0} \\ &+ 2u_{\mathbf{k}} v_{\mathbf{k}} \gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}1}^*] + \sum_{\mathbf{k}} [(\Delta_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}}^* + \Delta_{\mathbf{k}}^* u_{\mathbf{k}}^* v_{\mathbf{k}}) (\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0} + \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}1} - 1) \\ &+ (\Delta_{\mathbf{k}} v_{\mathbf{k}}^{*2} - \Delta_{\mathbf{k}}^* u_{\mathbf{k}}^{*2}) \gamma_{\mathbf{k}1} \gamma_{\mathbf{k}0} + (\Delta_{\mathbf{k}}^* v_{\mathbf{k}}^2 - \Delta_{\mathbf{k}} u_{\mathbf{k}}^2) \gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}1}^* + \Delta_{\mathbf{k}} b_{\mathbf{k}}^*] \end{aligned} \quad (3.43)$$

Now, if we choose $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ so that the coefficients of $\gamma_{\mathbf{k}1} \gamma_{\mathbf{k}0}$ and $\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}1}^*$ vanish, the hamiltonian is diagonalized; i.e., it is carried into a form containing only constants plus terms proportional to the occupation numbers $\gamma_{\mathbf{k}}^* \gamma_{\mathbf{k}}$. The coefficients of both undesired terms are zero if

$$2\xi_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} + \Delta_{\mathbf{k}}^* v_{\mathbf{k}}^2 - \Delta_{\mathbf{k}} u_{\mathbf{k}}^2 = 0$$

¹⁷N. N. Bogoliubov, *Nuovo Cimento* **7**, 794 (1958); *Zh. Eksperim. i Teor. Fiz.* **34**, 58 (1958) [*Soviet Phys.—JETP* **7**, 41 (1958)].

¹⁸J. G. Valatin, *Nuovo Cimento* **7**, 843 (1958).

When we multiply through by $\Delta_{\mathbf{k}}^*/u_{\mathbf{k}}^2$ and solve by the quadratic formula, this condition becomes

$$\frac{\Delta_{\mathbf{k}}^* v_{\mathbf{k}}}{u_{\mathbf{k}}} = (\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2)^{1/2} - \xi_{\mathbf{k}} \equiv E_{\mathbf{k}} - \xi_{\mathbf{k}} \quad (3.44)$$

using the definition of $E_{\mathbf{k}}$ introduced earlier. (We have chosen the positive sign of the square root so as to correspond to the stable solution of minimum rather than maximum energy.) Given the normalization requirement that $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$, and knowing that $|v_{\mathbf{k}}/u_{\mathbf{k}}| = (E_{\mathbf{k}} - \xi_{\mathbf{k}})/|\Delta_{\mathbf{k}}|$ from (3.44), we can solve for the coefficients and find

$$|v_{\mathbf{k}}|^2 = 1 - |u_{\mathbf{k}}|^2 = \frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right) \quad (3.35')$$

in exact agreement with (3.35), our variationally obtained result.

Although the phases of $u_{\mathbf{k}}$, $v_{\mathbf{k}}$, and $\Delta_{\mathbf{k}}$ are individually arbitrary, they are related by (3.44) since $\Delta_{\mathbf{k}}^* v_{\mathbf{k}}/u_{\mathbf{k}}$ is real. That is, the phase of $v_{\mathbf{k}}$ relative to $u_{\mathbf{k}}$ must be the phase of $\Delta_{\mathbf{k}}$. There is no loss in generality in choosing all the $u_{\mathbf{k}}$ to be real and positive. If we do so, $v_{\mathbf{k}}$ and $\Delta_{\mathbf{k}}$ must have the same phase.

3.5.1 Excitation Energies and the Energy Gap

With $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ chosen so as to diagonalize the model hamiltonian (3.43), the remaining terms reduce to

$$\mathcal{H}_M = \sum_{\mathbf{k}} (\xi_{\mathbf{k}} - E_{\mathbf{k}} + \Delta_{\mathbf{k}} b_{\mathbf{k}}^*) + \sum_{\mathbf{k}} E_{\mathbf{k}} (\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0} + \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}1}) \quad (3.45)$$

The first sum is a constant, which differs from the corresponding sum for the normal state at $T = 0$ ($E_{\mathbf{k}} = |\xi_{\mathbf{k}}|$, $\Delta_{\mathbf{k}} = 0$) by exactly the condensation energy (3.36) found earlier. This is natural since the BCS ground state is the vacuum state for the quasi-particle operators $\gamma_{\mathbf{k}}$. The second sum gives the increase in energy above the ground state in terms of the number operators $\gamma_{\mathbf{k}}^* \gamma_{\mathbf{k}}$ for the $\gamma_{\mathbf{k}}$ fermions. Thus, these $\gamma_{\mathbf{k}}$ describe the elementary quasi-particle excitations of the system, which are often called *Bogoliubons*. Evidently, the energies of these excitations are just

$$E_{\mathbf{k}} = (\xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2)^{1/2} \quad (3.46)$$

Thus, as we had anticipated, $\Delta_{\mathbf{k}}$ plays the role of an *energy gap* or minimum excitation energy since even at the Fermi surface, where $\xi_{\mathbf{k}} = 0$, $E_{\mathbf{k}} = |\Delta_{\mathbf{k}}| > 0$. Moreover, the notation $E_{\mathbf{k}}$ has now received its justification as the energy of an elementary excitation of momentum $\hbar\mathbf{k}$.

As in our earlier variational calculation, we require self-consistency when $\langle c_{-\mathbf{l}} c_{\mathbf{l}} \rangle$ computed from our solution is inserted back into (3.40). Rewriting the $c_{\mathbf{k}}$ operators in terms of the $\gamma_{\mathbf{k}}$, and dropping off-diagonal terms in quasi-

particle operators $\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}1}^*$ and $\gamma_{\mathbf{k}1} \gamma_{\mathbf{k}0}$ (since they do not contribute to averages), we have

$$\Delta_{\mathbf{k}} = - \sum_{\mathbf{l}} V_{\mathbf{kl}} \langle c_{-\mathbf{l}} c_{\mathbf{l}} \rangle = - \sum_{\mathbf{l}} V_{\mathbf{kl}} u_{\mathbf{l}}^* v_{\mathbf{l}} \langle 1 - \gamma_{\mathbf{l}0}^* \gamma_{\mathbf{l}0} - \gamma_{\mathbf{l}1}^* \gamma_{\mathbf{l}1} \rangle \quad (3.47)$$

At $T = 0$, when no quasi-particles are excited, this reduces to (3.27), so that exactly the same result (3.34) for $\Delta(0)$ in terms of $\hbar\omega_c$ and $N(0)V$ follows from the canonical transformation method as from the variational one. However, the present method is much more convenient for handling the extension of the calculation to $T > 0$.

3.6 FINITE TEMPERATURES

Since we have identified $E_{\mathbf{k}}$ as the *excitation* energy of a fermion quasi-particle, it must be a positive quantity $\geq \Delta$. The probability that it is excited in thermal equilibrium is the usual Fermi function

$$f(E_{\mathbf{k}}) = (e^{\beta E_{\mathbf{k}}} + 1)^{-1} \quad (3.48)$$

where $\beta = 1/kT$. Since $E_{\mathbf{k}} \geq \Delta$, $f(E_{\mathbf{k}})$ goes to zero at $T = 0$ for *all* \mathbf{k} , including $|\mathbf{k}| < k_F$. [In a parallel usage of $f(E_{\mathbf{k}})$ in the normal state, it would describe excitations from the $T = 0$ Fermi sea (i.e., holes inside and electrons outside the Fermi surface) rather than its common usage simply to describe the occupation of independent electron states.] In any case,

$$\langle 1 - \gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0} - \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}1} \rangle = 1 - 2f(E_{\mathbf{k}})$$

so that in general (3.47) becomes

$$\begin{aligned} \Delta_{\mathbf{k}} &= - \sum_{\mathbf{l}} V_{\mathbf{kl}} u_{\mathbf{l}}^* v_{\mathbf{l}} [1 - 2f(E_{\mathbf{l}})] \\ &= - \sum_{\mathbf{l}} V_{\mathbf{kl}} \frac{\Delta_{\mathbf{l}}}{2E_{\mathbf{l}}} \tanh \frac{\beta E_{\mathbf{l}}}{2} \end{aligned} \quad (3.49)$$

Making the BCS approximation that $V_{\mathbf{kl}} = -V$, we have $\Delta_{\mathbf{k}} = \Delta_{\mathbf{l}} = \Delta$, and the self-consistency condition becomes

$$\frac{1}{V} = \frac{1}{2} \sum_{\mathbf{k}} \frac{\tanh(\beta E_{\mathbf{k}}/2)}{E_{\mathbf{k}}} \quad (3.50)$$

where, as usual, $E_{\mathbf{k}} = (\xi_{\mathbf{k}}^2 + \Delta^2)^{1/2}$. Equation (3.50) determines the temperature dependence of the energy gap $\Delta(T)$.

3.6.1 Determination of T_c

The critical temperature T_c is the temperature at which $\Delta(T) \rightarrow 0$. In this case, $E_{\mathbf{k}} \rightarrow |\xi_{\mathbf{k}}|$, and the excitation spectrum becomes the same as in the normal state. Thus, T_c is found by replacing $E_{\mathbf{k}}$ with $|\xi_{\mathbf{k}}|$ in (3.50) and solving. After changing

the sum to an integral, taking advantage of the symmetry of $|\xi_{\mathbf{k}}|$ about the Fermi level, and changing to a dimensionless variable of integration, we find that this condition becomes

$$\frac{1}{N(0)V} = \int_0^{\beta_c \hbar \omega_c / 2} \frac{\tanh x}{x} dx$$

This integral can be evaluated and yields $\ln(A\beta_c \hbar \omega_c)$, where $A = 2e^\gamma / \pi \approx 1.13$ and γ here is Euler's constant $\gamma = 0.577\dots$. Consequently,

$$kT_c = \beta_c^{-1} = 1.13 \hbar \omega_c e^{-1/N(0)V} \quad (3.51)$$

Comparing this with (3.34), we see that

$$\frac{\Delta(0)}{kT_c} = \frac{2}{1.13} = 1.764 \quad (3.52)$$

so that the gap at $T = 0$ is indeed comparable in energy to kT_c . The numerical factor 1.76 has been tested in many experiments and found to be reasonable. That is, experimental values of 2Δ for different materials and different directions in k space generally fall in the range from $3.0kT_c$ to $4.5kT_c$, with most clustered near the BCS value of $3.5kT_c$.

3.6.2 Temperature Dependence of the Gap

Given (3.50), or its integral equivalent

$$\frac{1}{N(0)V} = \int_0^{\hbar \omega_c} \frac{\tanh \frac{1}{2} \beta (\xi^2 + \Delta^2)^{1/2}}{(\xi^2 + \Delta^2)^{1/2}} d\xi \quad (3.53)$$

$\Delta(T)$ can be computed numerically. For weak-coupling superconductors, in which $\hbar \omega_c / kT_c \gg 1$, $\Delta(T) / \Delta(0)$ is a universal function of T / T_c which decreases monotonically from 1 at $T = 0$ to zero at T_c , as shown in Fig. 3.2. Near $T = 0$, the temperature variation is exponentially slow since $e^{-\Delta/kT} \approx 0$, so that the hyperbolic tangent is very nearly unity and insensitive to T . Physically speaking, Δ is nearly constant until a significant number of quasi-particles are thermally excited. On the other hand, near T_c , $\Delta(T)$ drops to zero with a vertical tangent, approximately as

$$\frac{\Delta(T)}{\Delta(0)} \approx 1.74 \left(1 - \frac{T}{T_c}\right)^{1/2} \quad T \approx T_c \quad (3.54)$$

The variation of the order parameter Δ with the square root of $(T_c - T)$ is characteristic of all mean-field theories. For example, $M(T)$ has the same dependence in the molecular-field theory of ferromagnetism.

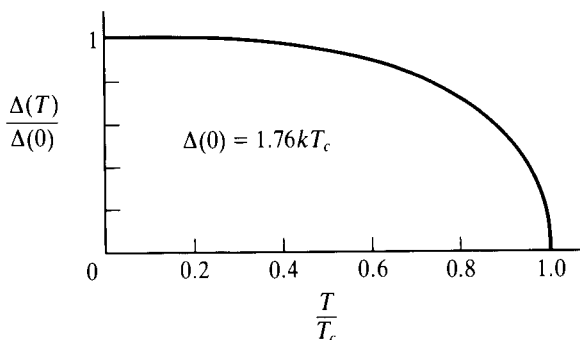


FIGURE 3.2

Temperature dependence of the energy gap in the BCS theory. Strictly speaking, this universal curve holds only in a weak-coupling limit, but it is a good approximation in most cases.

3.6.3 Thermodynamic Quantities

With $\Delta(T)$ determined, the temperature-dependent set of fermion excitation energies $E_{\mathbf{k}} = [\xi_{\mathbf{k}}^2 + \Delta(T)^2]^{1/2}$ is fixed. These energies determine the quasi-particle occupation numbers $f_{\mathbf{k}} = (1 + e^{\beta E_{\mathbf{k}}})^{-1}$, which in turn determine the electronic entropy in the usual way for a fermion gas, namely,

$$S_{es} = -2k \sum_{\mathbf{k}} [(1 - f_{\mathbf{k}}) \ln (1 - f_{\mathbf{k}}) + f_{\mathbf{k}} \ln f_{\mathbf{k}}] \quad (3.55)$$

Given $S_{es}(T)$, the specific heat can be written as

$$C_{es} = T \frac{dS_{es}}{dT} = -\beta \frac{dS_{es}}{d\beta}$$

Using (3.55), we have

$$\begin{aligned} C_{es} &= 2\beta k \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial \beta} \ln \frac{f_{\mathbf{k}}}{1 - f_{\mathbf{k}}} = -2\beta^2 k \sum_{\mathbf{k}} E_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}}{\partial \beta} \\ &= -2\beta^2 k \sum_{\mathbf{k}} E_{\mathbf{k}} \frac{df_{\mathbf{k}}}{d(\beta E_{\mathbf{k}})} \left(E_{\mathbf{k}} + \beta \frac{dE_{\mathbf{k}}}{d\beta} \right) \\ &= 2\beta k \sum_{\mathbf{k}} -\frac{\partial f_{\mathbf{k}}}{\partial E_{\mathbf{k}}} \left(E_{\mathbf{k}}^2 + \frac{1}{2}\beta \frac{d\Delta^2}{d\beta} \right) \end{aligned} \quad (3.56)$$

The first term is the usual one coming from the redistribution of quasi-particles among the various energy states as the temperature changes. The second term is more unusual and describes the effect of the temperature-dependent gap in changing the energy levels themselves.

Evidently, both terms in C_{es} will be exponentially small at $T \ll T_c$, where the minimum excitation energy Δ is much greater than kT . This accounts for the exponential form (1.13) noted earlier. Another interesting limit is very near T_c .

Then, as $\Delta(T) \rightarrow 0$, one can replace $E_{\mathbf{k}}$ by $|\xi_{\mathbf{k}}|$ in (3.56). The first term then reduces to the usual normal-state electronic specific heat

$$C_{en} = \gamma T = \frac{2\pi^2}{3} N(0) k^2 T \quad (3.57)$$

which is continuous at T_c . The second term is finite below T_c , where $d\Delta^2/dT$ is large, but it is zero above T_c , giving rise to a discontinuity ΔC in the electronic specific heat at T_c . The size of the discontinuity is readily evaluated by changing the sum to an integral, as follows:

$$\begin{aligned} \Delta C &= (C_{es} - C_{en}) \Big|_{T_c} = N(0) k \beta^2 \left(\frac{d\Delta^2}{d\beta} \right) \int_{-\infty}^{\infty} \left(\frac{-\partial f}{\partial |\xi|} \right) d\xi \\ &= N(0) \left(\frac{-d\Delta^2}{dT} \right) \Big|_{T_c} \end{aligned} \quad (3.58)$$

where we have used the fact that $\partial f / \partial |\xi| = \partial f / \partial \xi$ since $\partial f / \partial \xi$ is an even function of ξ . Using the approximate form (3.54) for $\Delta(T)$, with $\Delta(0) = 1.76kT_c$, we obtain $\Delta C = 9.4N(0)k^2T_c$. Comparing with (3.57), we find that the normalized magnitude of the discontinuity is

$$\frac{\Delta C}{C_{en}} = \frac{9.4}{2\pi^2/3} = 1.43 \quad (3.59)$$

The overall behavior of the electronic specific heat is sketched in Fig. 3.3*b*.

With $C_{es}(T)$ determined numerically from (3.56), we can integrate it to find the change in internal energy $U(T)$ as we decrease the temperature from T_c . At T_c , it must be the same as the normal value $U_{en}(0) - \frac{1}{2}\gamma T_c^2$ since the specific heat remains finite there. Thus,

$$U_{es}(T) = U_{en}(0) + \frac{1}{2}\gamma T_c^2 - \int_T^{T_c} C_{es} dT \quad (3.60)$$

From this and the entropy (3.55) we may then compute the free energy

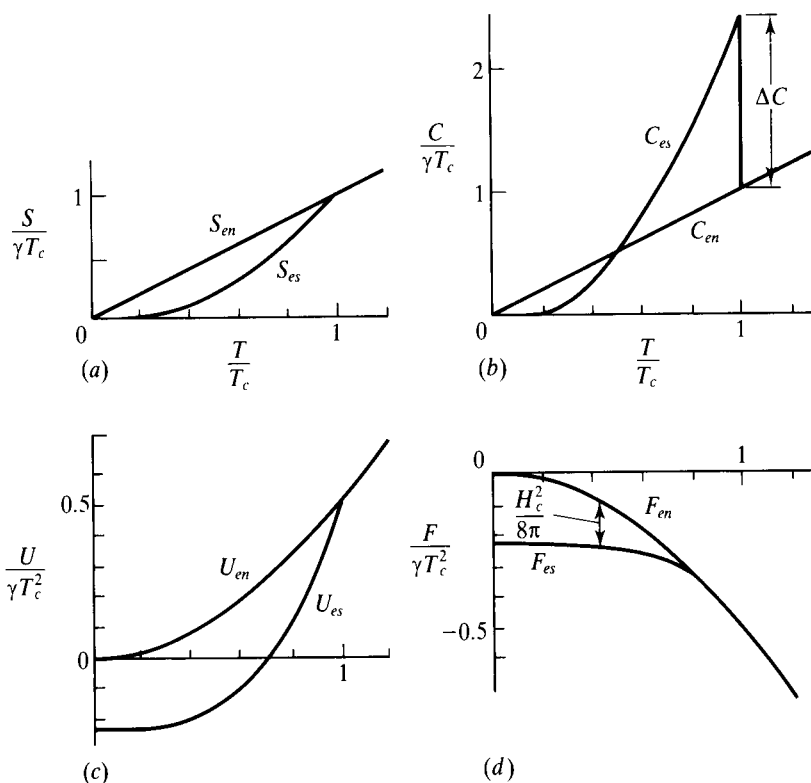
$$F_{es}(T) = U_{es}(T) - TS_{es}(T) \quad (3.61)$$

Assuming that the effect of the superconducting transition on the lattice free energy can be neglected, the thermodynamic critical field is then determined through the relation

$$\frac{H_c^2(T)}{8\pi} = F_{en}(T) - F_{es}(T) \quad (3.62)$$

where $F_{en}(T) = U_{en}(0) - \frac{1}{2}\gamma T^2$. These various thermodynamic quantities are plotted in Fig. 3.3. A useful numerical tabulation has been given by Mühlischlegel.¹⁹

¹⁹B. Mühlischlegel, *Z. Phys.* **155**, 313 (1959).

**FIGURE 3.3**

Comparison of thermodynamic quantities in superconducting and normal states. $U_{en}(0)$ is chosen as the zero of ordinates in (c) and (d). Because the transition is of second order, the quantities S , U , and F are continuous at T_c . Moreover, the slope of F_{es} joins continuously to that of F_{en} at T_c , since $\partial F/\partial T = -S$.

Since the critical-field curve $H_c(T)$ can be measured with greater accuracy than can typical thermodynamic quantities, it is of some importance to note that one can be derived from the other by rigorous thermodynamic computations, starting from (3.62). For example, the approximate parabolic temperature dependence of H_c quoted in (1.2) is inconsistent with an exponential variation of C_{es} , such as that quoted in (1.13), but it is consistent with a T^3 variation. Precise measurements of the deviation of $H_c(T)$ from the parabolic approximation have been used by Mapother²⁰ to test the BCS predictions of thermodynamic properties.

²⁰D. E. Mapother, *Phys. Rev.* **126**, 2021 (1962).

3.7 STATE FUNCTIONS AND THE DENSITY OF STATES

By inverting (3.42), we find the expressions

$$\begin{aligned}\gamma_{\mathbf{k}0}^* &= u_{\mathbf{k}}^* c_{\mathbf{k}\uparrow}^* - v_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow} \\ \gamma_{\mathbf{k}1}^* &= u_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow}^* + v_{\mathbf{k}}^* c_{\mathbf{k}\uparrow}\end{aligned}\quad (3.63)$$

for the $\gamma_{\mathbf{k}}^*$ operators, which create quasi-particle excitations of the two spin directions from the superconducting ground state, in terms of the electron creation operators $c_{\mathbf{k}}^*$. As remarked in connection with (3.45), the superconducting ground state $|\psi_G\rangle$ is defined as the vacuum state of the γ particles, i.e., by the relations

$$\gamma_{\mathbf{k}0}|\psi_G\rangle = \gamma_{\mathbf{k}1}|\psi_G\rangle = 0 \quad (3.64)$$

The structure of $|\psi_G\rangle$ in terms of the γ particles is of no interest, but it is of interest to demonstrate that in terms of the $c_{\mathbf{k}}$, it agrees with the BCS product form (3.14). This may be verified by considering, e.g.,

$$\gamma_{\mathbf{k}0}|\psi_G\rangle = (u_{\mathbf{k}}c_{\mathbf{k}\uparrow} - v_{\mathbf{k}}c_{-\mathbf{k}\downarrow}^*) \prod_{\mathbf{l}} (u_{\mathbf{l}} + v_{\mathbf{l}}c_{\mathbf{l}\uparrow}^*c_{-\mathbf{l}\downarrow}^*)|\phi_0\rangle$$

Multiplying out the factor involving the \mathbf{k} th pair, we find

$$u_{\mathbf{k}}^2 c_{\mathbf{k}\uparrow} + u_{\mathbf{k}} v_{\mathbf{k}} c_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* - v_{\mathbf{k}} u_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^* - v_{\mathbf{k}}^2 c_{-\mathbf{k}\downarrow}^* c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*$$

All these terms give zero when operating on $|\phi_0\rangle$ for the following reasons: the first is zero because the annihilation operator $c_{\mathbf{k}\uparrow}$ operates on the vacuum; the next two terms cancel because $c_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow}^*$ operating on the vacuum gives a factor of unity; the last term vanishes because it contains the same creation operator twice with no intervening annihilation operator. The case $\gamma_{\mathbf{k}1}|\psi_G\rangle$ works out similarly. Thus, (3.64) is verified, and the BCS form for the ground state is in exact agreement with that of the canonical-transformation method.

Now let us look at the excited states. For example, consider

$$\begin{aligned}\gamma_{\mathbf{k}0}^*|\psi_G\rangle &= (|u_{\mathbf{k}}|^2 c_{\mathbf{k}\uparrow}^* + u_{\mathbf{k}}^* v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^* - v_{\mathbf{k}}^* u_{\mathbf{k}} c_{-\mathbf{k}\downarrow} - |v_{\mathbf{k}}|^2 c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow}^*) \\ &\times \prod_{\mathbf{l} \neq \mathbf{k}} (u_{\mathbf{l}} + v_{\mathbf{l}} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^*)|\phi_0\rangle\end{aligned}$$

The two middle terms give zero for reasons mentioned earlier. The last term may be changed to $+|v_{\mathbf{k}}|^2 c_{\mathbf{k}\uparrow}^* c_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow}^*$ by using the anticommutation of the fermion operators, and then the factor $c_{-\mathbf{k}\downarrow} c_{-\mathbf{k}\downarrow}^*$ may be dropped since, operating on $|\phi_0\rangle$, it gives a factor of unity. Combining the remainder with the first term, we have

$$\gamma_{\mathbf{k}0}^*|\psi_G\rangle = c_{\mathbf{k}\uparrow}^* \prod_{\mathbf{l} \neq \mathbf{k}} (u_{\mathbf{l}} + v_{\mathbf{l}} c_{\mathbf{l}\uparrow}^* c_{-\mathbf{l}\downarrow}^*)|\phi_0\rangle \quad (3.65a)$$

Similarly,

$$\gamma_{\mathbf{k}\downarrow}^* |\psi_G\rangle = c_{-\mathbf{k}\downarrow}^* \prod_{l \neq \mathbf{k}} (u_l + v_l c_{l\uparrow}^* c_{-l\downarrow}^*) |\phi_0\rangle \quad (3.65b)$$

These are the excited states called *singles* in the original BCS treatment, where they were written down by inspection. They correspond to putting with certainty a single electron into one of the states of the pair $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$, while leaving with certainty the other state of the pair empty. This effectively blocks that pair state from participation in the many-body wavefunction and increases the system energy accordingly.

The operators $\gamma_{\mathbf{k}}^*$ change the expectation value of the electron number in the pair of states $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ from $2v_{\mathbf{k}}^2$ in the ground state to 1 in the excited state. The change is $(1 - 2v_{\mathbf{k}}^2) = u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2$, which ranges from -1 to $+1$ as $\xi_{\mathbf{k}}$ ranges from well below zero (inside Fermi surface) to well above zero (outside Fermi surface), as can be inferred²¹ from the plot of $v_{\mathbf{k}}^2$ in Fig. 3.1. This net change results from a probability $u_{\mathbf{k}}^2$ of a change by $+1$ and a probability $v_{\mathbf{k}}^2$ of a change by -1 . Such behavior would be inconsistent with exact number conservation in an isolated system. This apparent paradox is resolved by recalling that the $\gamma_{\mathbf{k}}^*$ operators are defined only with respect to a ground state having a definite phase of $\Delta_{\mathbf{k}}$, and such a state has a large uncertainty in N . If one wishes to consider excited states of an isolated system, one uses a prescription like (3.18) to project out the N -particle part *after* operating with the $\gamma_{\mathbf{k}}^*$ on $|\psi_G\rangle$. Note that $\gamma_{\mathbf{k}}^* |\psi_G\rangle$ has *no* component with an *even* number of particles. More generally, electron conservation requires that excitations always must be created or destroyed in pairs, as is expected for fermions. (It is for this reason that the *spectroscopic* gap is 2Δ , not Δ .) Considering, e.g., $\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}'0}^* |\psi_G\rangle$, and using (3.65a), we see that it has a well-defined N -particle projection

$$c_{\mathbf{k}\uparrow}^* c_{\mathbf{k}'\uparrow}^* \int_0^{2\pi} d\varphi e^{-i(N-2)\varphi/2} \prod_{l \neq \mathbf{k}, \mathbf{k}'} (|u_l| + |v_l| e^{i\varphi} c_{l\uparrow}^* c_{-l\downarrow}^*) |\phi_0\rangle \quad (3.66)$$

Anticipating the discussion of tunneling experiments, in which an excited state is created by actual addition or subtraction of an electron, we see that the state resulting from $\gamma_{\mathbf{k}0}^*$ operating on an N -electron system is

$$c_{\mathbf{k}\uparrow}^* \int d\varphi e^{-iN'\varphi/2} \prod_{l \neq \mathbf{k}} (|u_l| + |v_l| e^{i\varphi} c_{l\uparrow}^* c_{-l\downarrow}^*) |\varphi_0\rangle \quad (3.67)$$

where $N' = N$ if an electron is added, whereas $N' = N - 2$ if an electron is removed. Thus, we can always write out explicit expressions for these various excited states with a definite number of particles, although there is seldom any need to, except in the mesoscopic systems treated in Chap. 7. The important

²¹For more detail, see the discussion of *charge imbalance* in Sec. 11.2.

qualitative point is simply that pairs of electrons can be added to or subtracted from the condensate at will to achieve number conservation; for energy book-keeping purposes, such electrons are at the chemical potential μ .

To avoid the need to deal with explicit wavefunctions such as (3.66) and (3.67), let us follow Josephson²² in introducing an operator S which annihilates a Cooper pair, while S^* creates one. [For later reference in treating the Josephson effect, we note that S has the eigenvalue $e^{i\varphi}$ in a BCS state in which the phase of Δ (or of u^*v) is φ .] An equivalent operator p was also introduced by Bardeen.²³ We can then define a set of modified quasi-particle operators which definitely create either an electron or a hole, i.e., which either increase or decrease the number of electrons by one, whereas the $\gamma_{\mathbf{k}}^*$ operators of (3.63) create a linear combination of these possibilities. Thus, the two types of operators (3.63) are replaced by four:

$$\begin{aligned}\gamma_{e\mathbf{k}0}^* &= u_{\mathbf{k}}^* c_{\mathbf{k}\uparrow}^* - v_{\mathbf{k}}^* S^* c_{-\mathbf{k}\downarrow} \\ \gamma_{h\mathbf{k}0}^* &= u_{\mathbf{k}}^* S c_{\mathbf{k}\uparrow}^* - v_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow} \\ \gamma_{e\mathbf{k}1}^* &= u_{\mathbf{k}}^* c_{-\mathbf{k}\downarrow}^* + v_{\mathbf{k}}^* S^* c_{\mathbf{k}\uparrow} \\ \gamma_{h\mathbf{k}1}^* &= u_{\mathbf{k}}^* S c_{-\mathbf{k}\downarrow}^* + v_{\mathbf{k}}^* c_{\mathbf{k}\uparrow}\end{aligned}\quad (3.68)$$

Note that the hole and electron operators are related by

$$\gamma_{h\mathbf{k}}^* = S \gamma_{e\mathbf{k}}^* \quad (3.69)$$

which corresponds to the fact that creating a holelike excitation is equivalent to annihilating a pair and creating an electronlike excitation. Thus, these are not independent excitations but, rather, the same excitation with different numbers of condensed pairs. The distinctions embodied in (3.68) are essential in calculations²⁴ which distinguish transfer of charge from transfer of quasi-particles.

In dealing with tunneling processes which transfer electrons from one system to another, we need to reintroduce the chemical potential explicitly since it will differ between conductors maintained at different voltages. Because all our calculations of system energy have been referred to the chemical potential μ by subtracting μN_{op} , we simply add this back in and write

$$\mathcal{H} = \mu N_{\text{op}} + E_G + \sum_{\mathbf{k}} E_{\mathbf{k}} \gamma_{\mathbf{k}}^* \gamma_{\mathbf{k}} \quad (3.70)$$

where E_G is the ground-state energy and the sum runs over all the excitations. In view of (3.70), we see that the energy to create an electronlike excitation is $E_{e\mathbf{k}} = (E_{\mathbf{k}} + \mu)$, whereas that to create a hole is $E_{h\mathbf{k}} = (E_{\mathbf{k}} - \mu)$. In an isolated

²²B. D. Josephson, *Phys. Lett.* **1**, 251 (1962).

²³J. Bardeen, *Phys. Rev. Lett.* **9**, 147 (1962)

²⁴M. Tinkham, *Phys. Rev.* **B6**, 1747 (1972).

superconductor, the simplest number-conserving excitation consists of a hole and an electron, with total excitation energy

$$(E_{\mathbf{k}} + \mu) + (E_{\mathbf{k}'} - \mu) = E_{\mathbf{k}} + E_{\mathbf{k}'} \geq 2\Delta \quad (3.71)$$

On the other hand, in a tunneling process in which an electron is transferred from metal 1 to metal 2, conservation of energy requires that

$$(E_{\mathbf{k}_1} - \mu_1) + (E_{\mathbf{k}'_2} + \mu_2) = 0$$

so that

$$E_{\mathbf{k}_1} + E_{\mathbf{k}'_2} = (\mu_1 - \mu_2) = eV_{12} \quad (3.72)$$

It is of some historical interest to note that in the original form of the BCS theory it was necessary to give special treatment to *excited pairs* since the excited state formed by (3.66) with $\mathbf{k}'\uparrow$ replaced by $-\mathbf{k}\downarrow$ is not orthogonal to the ground state. As the appropriate orthogonal state is generated automatically by $\gamma_{\mathbf{k}_1}^* \gamma_{\mathbf{k}_0}^* |\psi_G\rangle$, however, no such special mathematical attention is required so long as excited states are expressed in terms of the $\gamma_{\mathbf{k}}^*$ operators.

3.7.1 Density of States

Now that we have seen that the quasi-particle excitations can be simply described as fermions created by the $\gamma_{\mathbf{k}}^*$, which are in one-to-one correspondence with the $c_{\mathbf{k}}^*$ of the normal metal, we can obtain the superconducting density of states $N_s(E)$ by equating

$$N_s(E) dE = N_n(\xi) d\xi$$

(Since we are thinking here of a single superconductor, we can safely revert to taking $\mu = 0$.) Because we are largely interested in energies ξ only a few millielectronvolts from the Fermi energy, we can take $N_n(\xi) = N(0)$, a constant. This leads directly to the simple result

$$\frac{N_s(E)}{N(0)} = \frac{d\xi}{dE} = \begin{cases} \frac{E}{(E^2 - \Delta^2)^{1/2}} & (E > \Delta) \\ 0 & (E < \Delta) \end{cases} \quad (3.73)$$

since $E_{\mathbf{k}}^2 = \Delta^2 + \xi_{\mathbf{k}}^2$. Excitations with all momenta \mathbf{k} , even those whose $\xi_{\mathbf{k}}$ fall in the gap, have their energies raised above Δ . Moreover, we expect a divergent state density just above $E = \Delta$, as indicated in Fig. 3.4. Of course, the total number of states is conserved because of the one-to-one correspondence between the $\gamma_{\mathbf{k}}$ and the $c_{\mathbf{k}}$. The nature of this correspondence is made more explicit by Fig. 3.5, which shows the relationship between the excitation energies in the normal and superconducting states.

It is worth noting that if the BCS model is followed literally, a narrow peak in the density of states occurs at the cutoff energy $\hbar\omega_c$ because above this energy, $\Delta = 0$ and $E_{\mathbf{k}} = \xi_{\mathbf{k}}$. As a result, $N(0)\Delta^2/2\hbar\omega_c$ extra states fall in an energy range of width $\Delta^2/2\hbar\omega_c$, causing a doubling of $N(E)$ in this range. Of course, this consequence of the model is not to be taken seriously since it depends critically

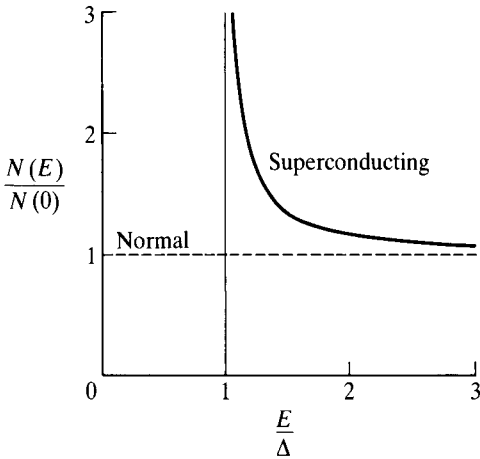


FIGURE 3.4

Density of states in superconducting compared to normal state. All \mathbf{k} states whose energies fall in the gap in the normal metal are raised in energy above the gap in the superconducting state.

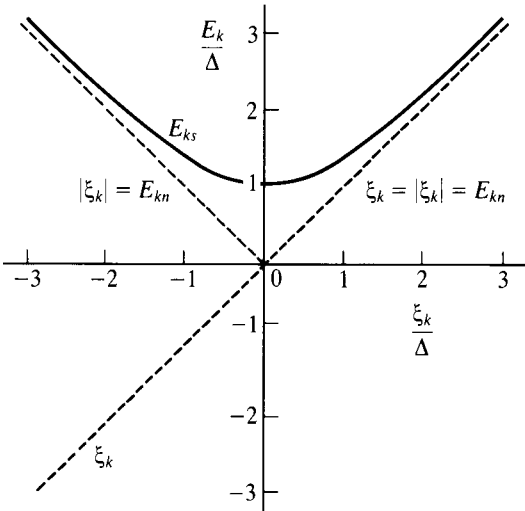


FIGURE 3.5

Energies of elementary excitations in the normal and superconducting states as functions of ξ_k , the independent-particle kinetic energy relative to the Fermi energy.

on the admittedly crude cutoff procedure. As described in the next section, a more rigorous treatment of the phonon-mediated interaction spreads this cutoff effect out over the entire energy range $\hbar\omega_c$, so that the actual departures from (3.73) are of order $(\Delta/\hbar\omega_c)^2$ or $(T_c/\Theta_D)^2$ to give about the same integrated effect.

3.8 ELECTRON TUNNELING

By far the most detailed experimental examination of the density of states is provided by electron tunneling. This technique was pioneered by Giaever,²⁵

²⁵I. Giaever, *Phys. Rev. Lett.* **5**, 147, 464 (1960).

who used it to confirm the density of states and temperature dependence of the energy gap predicted by BCS. The basic idea is that there is a nonzero probability of charge transfer by the quantum-mechanical tunneling of electrons between two conductors separated by a thin insulating barrier. This probability falls exponentially with the distance of separation and it depends on the details of the insulating material, but these aspects can be absorbed in a phenomenological tunneling matrix element $T_{\mathbf{k}\mathbf{q}}$. That is, we can assume a coupling term in the hamiltonian of the form

$$\mathcal{H}_T = \sum_{\sigma\mathbf{k}\mathbf{q}} T_{\mathbf{k}\mathbf{q}} c_{\mathbf{k}\sigma}^* c_{\mathbf{q}\sigma} + \text{herm conj} \quad (3.74)$$

where the subscript \mathbf{k} refers to one metal and \mathbf{q} to the other; we assume no spin flip in the tunneling process since there are no magnetic perturbations in the problem. The explicitly written term transfers an electron from metal \mathbf{q} to \mathbf{k} , whereas the conjugate term does the reverse. As usual, the transition probability (and hence the current) is proportional to the square of the matrix element, so long as we exclude the coherent processes of the Josephson tunneling.

If we consider, for example, an electron transferred by (3.74) into a state $\mathbf{k}\uparrow$ in a superconductor, we must reexpress this electron state in terms of the appropriate excitations, the $\gamma_{\mathbf{k}}$, using (3.68). The result is

$$c_{\mathbf{k}\uparrow}^* = u_{\mathbf{k}} \gamma_{e\mathbf{k}0}^* + v_{\mathbf{k}}^* \gamma_{h\mathbf{k}1} \quad (3.75)$$

If the superconductor is in its ground state, the second term gives zero, and the process contributes a current proportional to $|u_{\mathbf{k}}|^2 |T_{\mathbf{k}\mathbf{q}}|^2$. The physical significance of the factor $|u_{\mathbf{k}}|^2$ is that it is the probability that the state \mathbf{k} is *not* occupied in the BCS function, and hence is able to receive an incoming electron. Thus, it appears on the face of it that the tunneling current will depend on the nature of the superconducting ground state as well as on the density of available excited states; but this turns out not to be true. As is evident from Fig. 3.5, there is another state \mathbf{k}' having exactly the same energy $E_{\mathbf{k}'} = E_{\mathbf{k}}$, but with $\xi_{\mathbf{k}'} = -\xi_{\mathbf{k}}$. Using (3.75), with \mathbf{k} replaced by \mathbf{k}' we see that tunneling into \mathbf{k}' contributes a current proportional to $|u_{\mathbf{k}'}|^2 |T_{\mathbf{k}'\mathbf{q}}|^2 = |v_{\mathbf{k}}|^2 |T_{\mathbf{k}'\mathbf{q}}|^2$ since $|u(-\xi)| = |v(\xi)|$. Making the reasonable assumption that the two matrix elements are nearly equal since \mathbf{k} and \mathbf{k}' are both near the same point on the Fermi surface, the total current from these two channels is proportional to $(|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2) |T_{\mathbf{k}\mathbf{q}}|^2 = |T_{\mathbf{k}\mathbf{q}}|^2$, and the characteristic coherence factors of the superconducting wavefunction, $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$, have dropped out. If we now generalize to finite temperatures, so that the quasi-particle occupation numbers $f_{\mathbf{k}}$ are nonzero, both terms of (3.75) contribute, the first as $(1 - f_{\mathbf{k}})$, the second as $f_{\mathbf{k}}$. Again, when the degenerate channels are combined, the current is simply proportional to $|T_{\mathbf{k}\mathbf{q}}|^2$.

3.8.1 The Semiconductor Model

This disappearance of the coherence factors $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ makes it possible and convenient to reexpress the computation of the tunneling current in what is often called the *semiconductor model*. In this method, illustrated in Fig. 3.6, the normal metal is represented in the familiar elementary way as a continuous distribution of independent-particle energy states with density $N(0)$, including energies below as well as above the Fermi level. The superconductor is represented by an ordinary semiconductor with a density of independent-particle states obtained from Fig. 3.4 by adding its reflection on the negative-energy side of the chemical potential, so that it will reduce properly to the normal-metal density of states as $\Delta \rightarrow 0$. At $T = 0$, all states up to μ are filled; for $T > 0$, the occupation numbers are given by the Fermi function. It is worth noting that $f_{\mathbf{k}}$ now runs from 0 to 1, whereas in our previous convention, $f_{\mathbf{k}}$ ranged only from 0 to $\frac{1}{2}$ since $E_{\mathbf{k}} \gtrsim 0$. This difference reflects the fact that in the present model $f_{\mathbf{k}}$ measures a departure from the vacuum, whereas in the previous *excitation representation* it measured a departure from the ground state of the system.

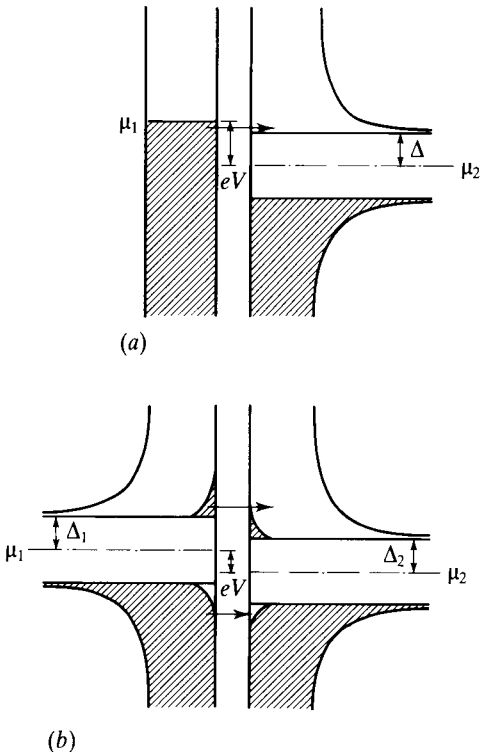


FIGURE 3.6

Example of semiconductor model description of electron tunneling. Density of states is plotted horizontally vs. energy vertically. Shading denotes states occupied by electrons. (a) *N-S* tunneling at $T = 0$, with bias voltage just above the conduction threshold, i.e., eV slightly exceeds the energy gap Δ . Horizontal arrow depicts electrons from the left tunneling into empty states on the right. (b) *S-S* tunneling at $T > 0$, with bias voltage below the threshold for conduction at $T = 0$, i.e., with $eV < \Delta_1 + \Delta_2$. Horizontal arrows depict tunneling involving thermally excited electrons or holes, respectively.

With this model, tunneling transitions are all *horizontal*, i.e., they occur at constant energy after adjusting the relative levels of μ in the two metals to account for the applied potential difference eV . This property facilitates summing up all contributions to the current in an elementary way since the various parallel channels noted earlier do not have to be considered anew in each case. Because this scheme so greatly simplifies the computations, we shall use it here to work out the tunneling characteristics of various types of junctions, and simply refer the reader to more detailed treatments which are available in the literature.²⁶ It should be borne in mind, however, that this technique to some extent *oversimplifies*. It is sound to treat the normal metal in this way, but it is less safe to conceal the mixing of hole and electron states which is present in the superconducting state even at $T = 0$. Although our previous argument for simply adding the currents from the two degenerate channels is valid for the usual case, there can be an interference effect between them which causes an oscillatory variation of the tunnel current with voltage or sample thickness known as the Tomasch effect.²⁷ Also, the method is inadequate for treating *charge-imbalance* regimes, where the states inside and outside the Fermi surface are not in equilibrium. (See Chap. 11.) These comments illustrate the need for caution in using the semiconductor model. Of course, this model also is inadequate for dealing with processes in which the condensed pairs play a role, since the ground state does not appear in the energy-level diagram.

Within the independent-particle approximation, the tunneling current from metal 1 to metal 2 can be written as

$$I_{1 \rightarrow 2} = A \int_{-\infty}^{\infty} |T|^2 N_1(E) f(E) N_2(E + eV) [1 - f(E + eV)] dE$$

where V is the applied voltage, eV is the resulting difference in the chemical potential across the junction, and $N(E)$ is the appropriate normal or superconducting density of states. The factors $N_1 f$ and $N_2(1 - f)$ give the numbers of occupied initial states and of available (i.e., empty) final states in unit energy interval. This expression assumes a constant tunneling-matrix element T (not to be confused with the temperature!); A is a constant of proportionality. Subtracting the reverse current, we obtain the net current

$$I = A |T|^2 \int_{-\infty}^{\infty} N_1(E) N_2(E + eV) [f(E) - f(E + eV)] dE \quad (3.76)$$

²⁶A particularly explicit discussion of the contributions of the various channels is given by M. Tinkham, *Phys. Rev.* **B6**, 1747 (1972). Earlier treatments and reviews have been given by M. H. Cohen, L. M. Falicov, and J. C. Phillips, *Phys. Rev. Lett.* **8**, 316 (1962); D. H. Douglass, Jr., and L. M. Falicov, in C. J. Gorter (ed.), *Progress in Low Temperature Physics*, vol. 4, North-Holland, Amsterdam (1964), p. 97; W. L. McMillan and J. M. Rowell, in R. D. Parks (ed.), *Superconductivity*, vol. 1, Dekker, New York (1969), Chap. 11.

²⁷W. J. Tomasch, *Phys. Rev. Lett.* **15**, 672 (1965); **16**, 16 (1966).

We shall now use this expression to treat a number of important cases.

3.8.2 Normal-Normal Tunneling

If both metals are normal, (3.76) becomes

$$\begin{aligned} I_{nn} &= A|T|^2 N_1(0)N_2(0) \int_{-\infty}^{\infty} [f(E) - f(E + eV)]dE \\ &= A|T|^2 N_1(0)N_2(0)eV \equiv G_{nn}V \end{aligned} \quad (3.77)$$

so that the junction is *ohmic*; i.e., it has a well-defined conductance G_{nn} , independent of V . Note that it is also independent of the temperature.

To help reduce any lingering confusion about the relation of this semiconductor, or independent-particle, scheme to the elementary excitation scheme, let us indicate how this simple case would have been treated in the other framework. First, at $T = 0$, all $f_{\mathbf{k}} = 0$, and there are no excitations present, both metals being in their Fermi-sea ground states. Thus, any tunneling process must involve creating two excitations, a hole in one metal and an electron in the other, the sum of the two excitation energies being eV , as given by (3.72). The resulting current is

$$\begin{aligned} I &= A|T|^2 \int_0^{eV} N_1(E)N_2(eV - E)dE \\ &= A|T|^2 N_1(0)N_2(0)eV \end{aligned}$$

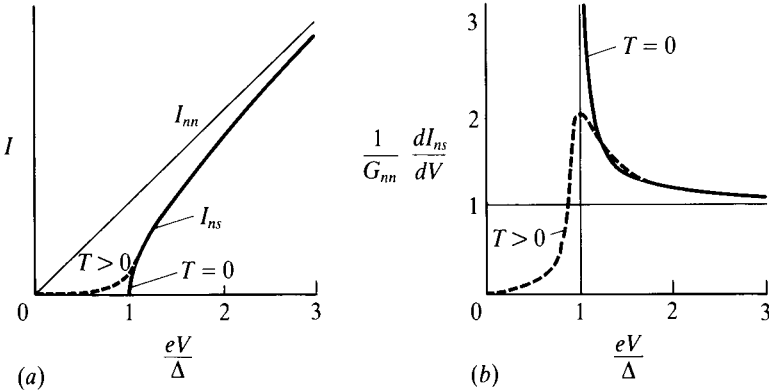
exactly as found in (3.77). For $T > 0$, the current from this process is reduced by the excitations already present, which block final states, but this effect is canceled by the extra current from the tunneling of the excitations, leading to a temperature-independent result.

3.8.3 Normal-Superconductor Tunneling

A more interesting case arises if one metal is superconducting. Then Fig. 3.6a is relevant, and (3.76) becomes

$$\begin{aligned} I_{ns} &= A|T|^2 N_1(0) \int_{-\infty}^{\infty} N_{2s}(E)[f(E) - f(E + eV)] dE \\ &= \frac{G_{nn}}{e} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_2(0)} [f(E) - f(E + eV)] dE \end{aligned} \quad (3.78)$$

In general, numerical means are required to evaluate this expression for the BCS density of states and thus to allow quantitative comparison with experiment, although the qualitative behavior is easily sketched. As indicated in Fig. 3.7a, at $T = 0$, there is no tunneling current until $e|V| \gtrsim \Delta$, since the chemical-potential difference must provide enough energy to create an excitation in the superconductor. The magnitude of the current is independent of the sign of V because


FIGURE 3.7

Characteristics of normal-superconductor tunnel junctions. (a) I - V characteristic. (b) Differential conductance. Solid curves refer to $T = 0$; dashed curves refer to a finite temperature.

hole and electron excitations have equal energies. For $T > 0$, the energy of excitations already present allows them to tunnel at lower voltages, giving an exponential tail of the current in the region below $eV = \Delta$.

A more direct comparison of theory and experiment can be made if one considers the differential conductance dI/dV as a function of V . From (3.78)

$$G_{ns} = \frac{dI_{ns}}{dV} = G_{nn} \int_{-\infty}^{\infty} \frac{N_{2s}(E)}{N_2(0)} \left[-\frac{\partial f(E + eV)}{\partial(eV)} \right] dE \quad (3.79)$$

Since $-\partial f(E + eV)/\partial(eV)$ is a bell-shaped weighting function peaked at $E = -eV$, with width $\sim 4kT$ and unit area under the curve, it is clear that as $kT \rightarrow 0$, this approaches

$$G_{ns} \Big|_{T=0} = \frac{dI_{ns}}{dV} \Big|_{T=0} = G_{nn} \frac{N_{2s}(e|V|)}{N_2(0)} \quad (3.80)$$

Thus, in the low-temperature limit, the differential conductance measures directly the density of states. At finite temperatures, as shown in Fig. 3.7b, the conductance measures a density of states smeared by $\sim \pm 2kT$ in energy, due to the width of the weighting function. Because this function has exponential “skirts,” it turns out that the differential conductance at $V = 0$ is related exponentially to the width of the gap. In the limit $kT \ll \Delta$, this relation reduces to

$$\frac{G_{ns}}{G_{nn}} \Big|_{V=0} = \left(\frac{2\pi\Delta}{kT} \right)^{1/2} e^{-\Delta/kT} \quad (3.81)$$

3.8.4 Superconductor-Superconductor Tunneling

If both metals are superconducting, the energy-level structure is as shown in Fig. 3.6*b* and (3.76) becomes

$$\begin{aligned}
 I_{ss} &= \frac{G_{nn}}{e} \int_{-\infty}^{\infty} \frac{N_{1s}(E)}{N_1(0)} \frac{N_{2s}(E+eV)}{N_2(0)} [f(E) - f(E+eV)] dE \\
 &= \frac{G_{nn}}{e} \int_{-\infty}^{\infty} \frac{|E|}{[E^2 - \Delta_1^2]^{1/2}} \frac{|E+eV|}{[(E+eV)^2 - \Delta_2^2]^{1/2}} [f(E) - f(E+eV)] dE \quad (3.82)
 \end{aligned}$$

In the second form, it is understood that the range of integration excludes values of E such that $|E| < |\Delta_1|$ and $|E+eV| < |\Delta_2|$. Again numerical integration is required to compute complete I - V curves. However, the qualitative features are indicated in Fig. 3.8. At $T=0$, no current can flow until $eV = \Delta_1 + \Delta_2$; at this point, the potential difference supplies enough energy to create a hole on one side and a particle on the other. Since the density of states is infinite at the gap edges, it turns out that there is a discontinuous jump in I_{ss} at $eV = \Delta_1 + \Delta_2$, even at finite temperatures. At $T > 0$, current also flows at lower voltages because of the availability of thermally excited quasi-particles. This current rises sharply to a peak when $eV = |\Delta_1 - \Delta_2|$ because this voltage provides just the energy to allow thermally excited quasi-particles in the peak of the density of states at Δ_1 , say, to tunnel into the peaked density of available states at Δ_2 . The existence of this peak leads to a *negative-resistance region* [$dI/dV < 0$] for $|\Delta_1 - \Delta_2| \leq eV \leq \Delta_1 + \Delta_2$. This region cannot be observed with the usual current-source arrangement since there are three possible values of V for given I and the one with $dI/dV < 0$ is unstable. A voltage source must be used to maintain stable operation. The existence of sharp features at both $|\Delta_1 - \Delta_2|$ and $\Delta_1 + \Delta_2$ allows very convenient determinations of $\Delta_1(T)$ and $\Delta_2(T)$ from the tunneling curves. The S - S tunneling method is superior to the N - S tunneling method in this

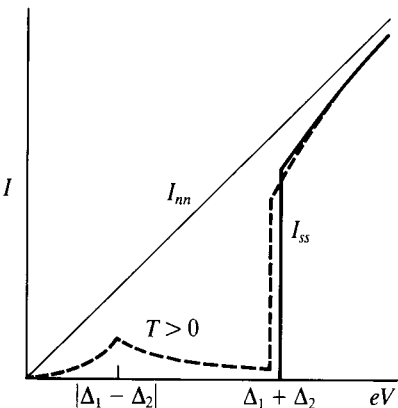


FIGURE 3.8

Superconductor-superconductor tunneling characteristic. Note that for $T > 0$ there are sharp features corresponding to both the sum and the difference of the two gap values. The peak at $|\Delta_1 - \Delta_2|$ would actually be a logarithmic singularity in the absence of gap anisotropy and level broadening due to lifetime effects.

regard because the existence of very sharply peaked densities of states at the gap edges of both materials helps to counteract the effects of thermal smearing.

3.8.5 Phonon Structure

When tunneling curves are measured in materials with strong electron-phonon coupling, structure beyond that outlined above is quite readily observed. Giaever et al.²⁸ noticed this first in lead and remarked that the structure occurred near energies that were characteristic of the phonon structure. This observation has since been greatly refined, from both experimental and theoretical viewpoints. The key point, made by Schrieffer, Scalapino, and Wilkins,²⁹ is that the observed density of states should be

$$N_s(E) = N(0)\text{Re} \frac{E}{[E^2 - \Delta^2(E)]^{1/2}} \quad (3.83)$$

where Re indicates the real part of the expression that follows. This reduces to our earlier result (3.73) if Δ can be taken to be real and constant, as in the simple BCS model, but in the strong-coupling theory Δ becomes complex and energy dependent. The resulting energy-dependent phase of $\Delta(E)$ has physical content and is entirely distinct from the single arbitrary phase choice of Δ within the BCS approximation. The imaginary part of Δ corresponds to a damping of the quasi-particle excitations by decay with creation of real phonons; hence, it is large when $E \approx \hbar\omega_{ph}$. There is a corresponding resonant variation of Re Δ . Such behavior is, of course, hardly surprising given our model in which the interaction causing superconductivity is phonon-mediated. The simple BCS approximation suppresses these details caused by the retarded nature of the interaction [apart from the crude manifestation of a narrow peak in $N(E)$ at $\hbar\omega_c$, mentioned at the end of Sec. 3.7], but the more exact Eliashberg³⁰ procedure appears to give a quantitative account of the observed phenomena. This agreement between theory and experiment in such materials as lead and mercury has eliminated any remaining doubt of the correctness of the electron-phonon mechanism for superconductivity in these materials.

The central quantity in this analysis is $\alpha^2F(\omega)$, i.e., the product of the electron-phonon coupling strength and the density of phonon states, both as functions of energy. A comprehensive review of microscopic calculations of

²⁸I. Giaever, H. R. Hart, and K. Megerle, *Phys. Rev.* **126**, 941 (1962).

²⁹J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, *Phys. Rev. Lett.* **10**, 336 (1963); *Phys. Rev.* **148**, 263 (1966).

³⁰G. M. Eliashberg, *Zh. Eksperim. i Teor. Fiz.* **38**, 966 (1960) [*Soviet Phys.—JETP* **11**, 696 (1960)].

$\alpha^2 F(\omega)$ for many materials has been given by Carbotte.³¹ Working from the experimental side, McMillan and Rowell³² were very successful in inverting the tunneling data to find the spectrum of $\alpha^2 F(\omega)$. Their results generally agree well with expectations based on neutron scattering from phonons where such data are available. In fact, the tunneling data give results of superior accuracy for features such as the location of van Hove singularities in the phonon density of states, which appear as peaks in the experimentally obtained trace of the second derivative of the tunneling current.

3.9 TRANSITION PROBABILITIES AND COHERENCE EFFECTS

The effect of an external perturbation on the electrons in a metal can be expressed in terms of an interaction hamiltonian

$$\mathcal{H}_1 = \sum_{\mathbf{k}\sigma, \mathbf{k}'\sigma'} B_{\mathbf{k}'\sigma', \mathbf{k}\sigma} c_{\mathbf{k}'\sigma'}^* c_{\mathbf{k}\sigma} \quad (3.84)$$

where the $B_{\mathbf{k}'\sigma', \mathbf{k}\sigma}$ are matrix elements of the perturbing operator between the ordinary one-electron states of the normal metal. In the normal state, each term in this sum is independent and the square of each $B_{\mathbf{k}'\sigma', \mathbf{k}\sigma}$ is proportional to a corresponding transition probability. This is not the case in the superconducting state, however, because it consists of a phase-coherent superposition of occupied one-electron states. As a result, there are interference terms which are not present in the normal state.

This can be seen in detail by expanding the terms in (3.84) using the γ operators. It is then seen that the terms $c_{\mathbf{k}'\sigma'}^* c_{\mathbf{k}\sigma}$ and $c_{-\mathbf{k}-\sigma}^* c_{-\mathbf{k}'-\sigma'}$ connect the same quasi-particle states. For example,

$$c_{\mathbf{k}'\uparrow}^* c_{\mathbf{k}\uparrow} = u_{\mathbf{k}'} u_{\mathbf{k}}^* \gamma_{\mathbf{k}'0}^* \gamma_{\mathbf{k}0} - v_{\mathbf{k}'} v_{\mathbf{k}} \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}'1} + u_{\mathbf{k}'} v_{\mathbf{k}} \gamma_{\mathbf{k}'0}^* \gamma_{\mathbf{k}1} + v_{\mathbf{k}'} u_{\mathbf{k}}^* \gamma_{\mathbf{k}'1} \gamma_{\mathbf{k}0} \quad (3.85a)$$

and

$$c_{-\mathbf{k}\downarrow}^* c_{-\mathbf{k}'\downarrow} = -v_{\mathbf{k}'} v_{\mathbf{k}} \gamma_{\mathbf{k}'0}^* \gamma_{\mathbf{k}0} + u_{\mathbf{k}} u_{\mathbf{k}'}^* \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}'1} + u_{\mathbf{k}} v_{\mathbf{k}'} \gamma_{\mathbf{k}'0}^* \gamma_{\mathbf{k}1} + v_{\mathbf{k}} u_{\mathbf{k}'}^* \gamma_{\mathbf{k}'1} \gamma_{\mathbf{k}0} \quad (3.85b)$$

Thus, it is clear that matrix elements of these two terms in (3.84) must be added *before* squaring since they add coherently in determining the transition rate.

Fortunately, this addition can be done quite readily since one expects the coefficients $B_{\mathbf{k}'\sigma', \mathbf{k}\sigma}$ and $B_{-\mathbf{k}-\sigma, -\mathbf{k}'-\sigma'}$ to differ at most in sign because both

³¹J. Carbotte, *Revs. Mod. Phys.* **62**, 1027 (1990).

³²W. L. McMillan and J. M. Rowell, *Phys. Rev. Lett.* **14**, 108 (1965); see also J. M. Rowell and L. Kopf, *Phys. Rev.* **137**, A907 (1965). An excellent review is given by McMillan and Rowell in R. D. Parks (ed.), *Superconductivity*, Dekker, New York (1969), Chap. 11.

represent processes in which the momentum change of the electron is $\mathbf{k}' - \mathbf{k}$ and its spin change is $\sigma' - \sigma$. Thus, these terms can be combined as

$$B_{\mathbf{k}'\sigma', \mathbf{k}\sigma} (c_{\mathbf{k}'\sigma'}^* c_{\mathbf{k}\sigma} \pm c_{-\mathbf{k}-\sigma}^* c_{-\mathbf{k}'-\sigma'}) \quad (3.86)$$

where the sign choice depends on the nature of \mathcal{H}_1 .

As shown by BCS, there are two cases. Case I is typified by the electron-phonon interaction responsible for ultrasonic attenuation. Being the interaction of the electron with a simple scalar deformation potential, it depends only on the momentum change; it is independent of the sense of \mathbf{k} or σ , and the two matrix elements have the same sign and add coherently. Case II is typified by the interaction of the electron with the electromagnetic field via a term $\mathbf{p} \cdot \mathbf{A}$; since this changes sign on replacing \mathbf{k} by $-\mathbf{k}$, the negative sign in (3.86) is appropriate.

Neither of these two interactions has involved the spin, so that we have had $\sigma = \sigma'$. If there is a spin change, as with terms of the sort $I_+ S_-$ in the hyperfine interaction of the electron with a nucleus, the sign associations are formally reversed. Following BCS, we indicate this with a factor $\Theta_{\sigma\sigma'}$, which is ± 1 for $\sigma' = \pm\sigma$. Thus, upon collecting terms and taking $u_{\mathbf{k}}$, $v_{\mathbf{k}}$, and Δ real, we see that (3.86) becomes

$$B_{\mathbf{k}'\sigma', \mathbf{k}\sigma} [(u_{\mathbf{k}'} u_{\mathbf{k}} \mp v_{\mathbf{k}'} v_{\mathbf{k}}) (\gamma_{\mathbf{k}'\sigma'}^* \gamma_{\mathbf{k}\sigma} \pm \Theta_{\sigma'\sigma} \gamma_{-\mathbf{k}-\sigma}^* \gamma_{-\mathbf{k}'-\sigma'}) \\ + (v_{\mathbf{k}} u_{\mathbf{k}'} \pm u_{\mathbf{k}} v_{\mathbf{k}'}) (\gamma_{\mathbf{k}'\sigma'}^* \gamma_{-\mathbf{k}-\sigma}^* \pm \Theta_{\sigma'\sigma} \gamma_{-\mathbf{k}'-\sigma'} \gamma_{\mathbf{k}\sigma})] \quad (3.87)$$

(To facilitate writing this out for general spin directions, we have used a slightly modified notation, in which $\gamma_{\mathbf{k}\sigma} = \gamma_{\mathbf{k}0}$ for $\sigma = \uparrow$, and $\gamma_{\mathbf{k}\sigma} = \gamma_{-\mathbf{k}1}$ for $\sigma = \downarrow$.) From this expansion we see that the factor $\Theta_{\sigma\sigma'}$ really has no effect on the magnitude of transition probabilities; it affects only the relative phase of off-diagonal matrix elements connecting disparate states. The decisive point is whether the interaction is of case I or II, corresponding to the upper and lower signs in the coherence factors, i.e., the combinations of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ in (3.87). For example, although the part $I_+ S_z$ of the hyperfine coupling does not flip the spin, and hence has $\Theta_{\sigma\sigma'} = +1$ rather than -1 as above for $I_+ S_-$, both terms are governed by case II coherence factors because they are odd with respect to reversal of the spin. Generalizing from these examples, we see that cases I and II pertain to perturbations which are even and odd, respectively, under time reversal of the electronic states, which interchanges the partners in the Cooper-pairing scheme.

From (3.87) we see that in the computation of transition probabilities, the squared matrix elements $|B_{\mathbf{k}'\sigma', \mathbf{k}\sigma}|^2$ will be multiplied by so-called *coherence factors*, namely, $(uu' \mp vv')^2$ for the scattering of quasi-particles, and $(vu' \pm uv')^2$ for the creation or annihilation of two quasi-particles. (We have made an obvious condensation of the notation here.) With u and v given by (3.35), these coherence factors can be evaluated as explicit functions of energy. For example,

$$\begin{aligned}
(uu' \mp vv')^2 &= \frac{1}{4} \left\{ \left[\left(1 + \frac{\xi}{E} \right) \left(1 + \frac{\xi'}{E'} \right) \right]^{1/2} \mp \left[\left(1 - \frac{\xi}{E} \right) \left(1 - \frac{\xi'}{E'} \right) \right]^{1/2} \right\}^2 \\
&= \frac{1}{4} \left\{ \left(1 + \frac{\xi}{E} + \frac{\xi'}{E'} + \frac{\xi\xi'}{EE'} \right) + \left(1 - \frac{\xi}{E} - \frac{\xi'}{E'} + \frac{\xi\xi'}{EE'} \right) \right. \\
&\quad \left. \mp 2 \left[\left(1 - \frac{\xi^2}{E^2} \right) \left(1 - \frac{\xi'^2}{E'^2} \right) \right]^{1/2} \right\} = \frac{1}{2} \left(1 + \frac{\xi\xi'}{EE'} \mp \frac{\Delta^2}{EE'} \right)
\end{aligned}$$

Since E is an even function of ξ , when we sum over $\xi_{\mathbf{k}}$, terms appear in pairs such that the terms odd in ξ or ξ' cancel. Thus, effectively the coherence factor for scattering is

$$(uu' \mp vv')^2 = \frac{1}{2} \left(1 \mp \frac{\Delta^2}{EE'} \right) \quad (3.88a)$$

Similarly, the coherence factor for creation or annihilation of a pair of quasi-particles is

$$(vu' \pm uv')^2 = \frac{1}{2} \left(1 \pm \frac{\Delta^2}{EE'} \right) \quad (3.88b)$$

It is convenient to note that in the *semiconductor-model* sign convention, in which one of each pair of quasi-particles created or destroyed is assigned a negative energy, the coherence factors for both scattering and pair creation have the same form

$$F(\Delta, E, E') = \frac{1}{2} \left(1 \mp \frac{\Delta^2}{EE'} \right) \quad (3.89)$$

where the upper sign corresponds to case I and the lower to case II.

Evidently, the greatest effect of these coherence factors is for energies E and E' near the gap edge Δ , in which case (3.89) is either ~ 0 or ~ 1 , depending on the sign. If one considers low-energy scattering processes for $\hbar\omega \ll \Delta$, no quasi-particles are created, so E and E' have the same sign. Then for case I processes like ultrasonic attenuation, $F \ll 1$, whereas for case II processes like nuclear relaxation, $F \sim 1$. The situation is reversed for high-energy processes with $\hbar\omega \gtrsim 2\Delta$, which create pairs of quasi-particles. Then $F \sim 1$ for case I processes and $F \ll 1$ for case II processes. Of course, if E and $E' \gg \Delta$, there is little difference between case I and II, and the superconducting coherence is unimportant.

These general considerations are made more clear by considering examples of the calculation of transition rates. Following the same line of argument used in

reaching (3.76) for the case of tunneling, we expect a net transition rate between energy levels E and $E' = E + \hbar\omega$ to be proportional to

$$\alpha_s = \int |M|^2 F(\Delta, E, E + \hbar\omega) N_s(E) N_s(E + \hbar\omega) \times [f(E) - f(E + \hbar\omega)] dE \quad (3.90)$$

where M is the magnitude of a suitable one-electron matrix element. Since we shall always be interested in ratios to the normal-state values, we do not need to know more about the actual value of M . Upon inserting the explicit expressions for N_s and F , and simplifying, we find that (3.90) becomes

$$\alpha_s = |M|^2 N^2(0) \int_{-\infty}^{\infty} \frac{|E(E + \hbar\omega) \mp \Delta^2| [f(E) - f(E + \hbar\omega)]}{(E^2 - \Delta^2)^{1/2} [(E + \hbar\omega)^2 - \Delta^2]^{1/2}} dE$$

where it is understood that the regions with $|E|$ or $|E + \hbar\omega| < \Delta$ are excluded from the integration. In the normal state, $\Delta = 0$, and the corresponding expression reduces to $\alpha_n = |M|^2 N^2(0) \hbar\omega$. Thus, the desired ratio is

$$\frac{\alpha_s}{\alpha_n} = \frac{1}{\hbar\omega} \int_{-\infty}^{\infty} \frac{|E(E + \hbar\omega) \mp \Delta^2| [f(E) - f(E + \hbar\omega)]}{(E^2 - \Delta^2)^{1/2} [(E + \hbar\omega)^2 - \Delta^2]^{1/2}} dE \quad (3.91)$$

with the upper sign referring to case I processes and the lower to case II. We now use this general expression to treat some important specific cases.

3.9.1 Ultrasonic Attenuation

As noted earlier, the relevant matrix elements for treating the attenuation of longitudinal sound waves have case I coherence factors, i.e., the upper sign in (3.91). (We restrict our attention to longitudinal waves to avoid the complications which arise in the transverse case because currents are generated which are screened electromagnetically, giving a mixture of effects.) We note further that in typical ultrasonic experiments the sound frequency is less than 10^9 Hz, so that $\hbar\omega \lesssim 10^{-2} \Delta(0)$; also, $\hbar\omega \ll kT$. These inequalities enable us to consider only a simple low-frequency limiting case. Inspecting (3.91) in the limit as $\hbar\omega \rightarrow 0$, we see that most factors cancel, leaving

$$\begin{aligned} \frac{\alpha_s}{\alpha_n} &= \lim_{\hbar\omega \rightarrow 0} \frac{1}{\hbar\omega} \int [f(E) - f(E + \hbar\omega)] dE \\ &= - \int \frac{\partial f}{\partial E} dE \end{aligned}$$

with the integration extending from $-\infty$ to $-\Delta$ and from Δ to ∞ . Thus,

$$\begin{aligned}\frac{\alpha_s}{\alpha_n} &= f(-\infty) - f(-\Delta) + f(\Delta) - f(\infty) \\ &= 2f(\Delta) = \frac{2}{1 + e^{\Delta/kT}}\end{aligned}\quad (3.92)$$

This very simple result, combined with our previous calculation of $\Delta(T)$, predicts the behavior shown in Fig. 3.9. In particular, the infinite slope of $\Delta(T)$ at T_c causes α_s/α_n to drop with infinite slope as T is lowered below T_c . On the other hand, for $T \ll T_c$, the excess of α_s/α_n above a residual value due to nonelectronic mechanisms becomes exponentially small as the number of thermally excited quasi-particles available to absorb energy goes to zero.

When it is possible to carry experiments to low enough values of T/T_c to establish the residual attenuation level quite exactly, one can infer a value of $\Delta(T)$ from the attenuation data using (3.92). In fact, by propagating sound in different directions in single crystals, Morse and coworkers³³ were among the first to be able to get some measure of the anisotropy of the gap $\Delta_{\mathbf{k}}$ with respect to crystal-line axes. This technique suffers from the fact that a given direction of sound propagation $\hat{\mathbf{k}}_s$ measures an average of $\Delta_{\mathbf{k}}$ over a disk perpendicular to $\hat{\mathbf{k}}_s$. The reason for this is that for efficient energy transfer between the sound wave and the electrons, the component of quasi-particle velocity parallel to $\hat{\mathbf{k}}_s$ must equal the sound velocity. Since $v_{\text{sound}} \ll v_{\text{electron}}$, this means that only electrons moving almost perpendicular to $\hat{\mathbf{k}}_s$ are effective in the attenuation. Nonetheless, values

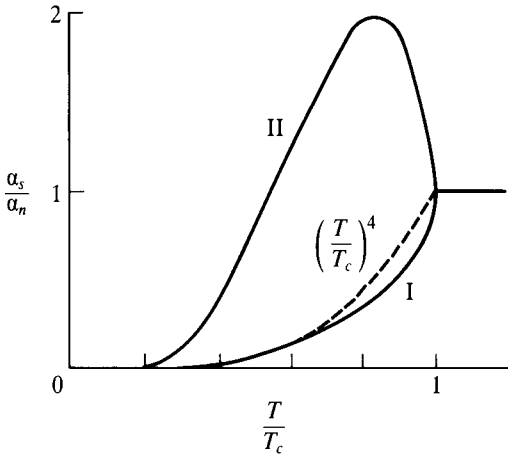


FIGURE 3.9

Temperature dependence of low-frequency absorption processes obeying case I and II coherence factors, compared with the $(T/T_c)^4$ dependence that might be expected for *all* processes from a simple two-fluid model. The curve for case I applies to ultrasonic attenuation, and it is a well-defined low-frequency limit. The curve for case II, which applies to nuclear relaxation or electromagnetic absorption, has no well-defined low-frequency limit unless gap anisotropy or level broadening is taken into account. The curve drawn here corresponds to a broadening of about $0.02\Delta(0)$.

³³R. W. Morse, "Ultrasonic Attenuation in Metals at Low Temperatures," in K. Mendelssohn (ed.) *Progress in Cryogenics*, vol. I, Heywood, London (1959), p. 219.

of $2\Delta(0)$ in tin ranging from $3.3kT_c$ to $3.9kT_c$ have been inferred from such measurements, e.g., by Claiborne and Einspruch.³⁴ Phillips³⁵ has carefully re-examined the detailed nature of elastic scattering in anisotropic superconductors and concluded that some earlier discussions were oversimplified.

The complication of electromagnetic screening of transverse sound waves mentioned earlier can be put to good use as a means of measuring the penetration depth very near T_c , where it approaches infinity. The point is that the screening becomes essentially complete as soon as $\lambda(T)$ is less than the ultrasonic wavelength, so that the electrodynamic attenuation becomes negligible for lower temperatures, leading to a very sharp drop in attenuation within less than 1 percent of T_c . Using this effect, Fossheim³⁶ obtained what are probably the most reliable available values for λ of indium from measurements of α_s/α_n within a few millidegrees of T_c .

Another complication which can enter ultrasonic-attenuation measurements arises from the electronic damping of the motion of dislocations driven by the sound waves.³⁷ Because of dislocation pinning effects, this leads to a nonlinear response which makes definition of α_s/α_n difficult except at very low signal levels. Mason³⁸ showed that when these effects were taken into account, the apparently anomalous measurements on lead³⁹ could be reconciled with expectations based on a gap $2\Delta(0) = 4.1kT_c$, a value in reasonable agreement with results from other techniques.

3.9.2 Nuclear Relaxation

The matrix elements for nuclear-spin relaxation by interaction with quasi-particles have the case II coherence factor, which corresponds to *constructive* interference in the relevant low-energy scattering processes. This causes the relaxation rate $1/T_1$ to *rise* above the normal value upon cooling through T_c before it eventually goes exponentially to zero, as it must when all quasi-particles above the gap are "frozen out." This behavior, sketched in Fig 3.9 and confirmed experimentally by Hebel and Slichter,⁴⁰ is in sharp contrast with the *drop* with vertical tangent found in the case of ultrasonic attenuation. The ability of the BCS pairing theory, with its coherence factors, to explain this difference in a natural

³⁴L. T. Claiborne and N. G. Einspruch, *Phys. Rev. Lett.* **15**, 862 (1965).

³⁵W. A. Phillips, *Proc. Roy. Soc.* **A309**, 259 (1969).

³⁶K. Fossheim, *Phys. Rev. Lett.* **19**, 81 (1967).

³⁷B. R. Tittman and H. E. Bömmel, *Phys. Rev.* **151**, 178 (1965).

³⁸W. P. Mason, *Phys. Rev.* **143**, 229 (1966).

³⁹R. E. Love, R. W. Shaw, and W. A. Fate, *Phys. Rev.* **138**, A1453 (1965).

⁴⁰L. C. Hebel and C. P. Slichter, *Phys. Rev.* **107**, 901 (1957); **113**, 1504 (1959); L. C. Hebel, *Phys. Rev.* **116**, 79 (1959).

way was one of the key triumphs which validated the theory. By way of contrast, any simple “two-fluid” model which attributed the ultrasonic attenuation and nuclear relaxation to a certain fraction of “normal electrons” would have to give the same temperature dependence for all such properties. For example, one might expect a normal-electron density $n_n/n = (T/T_c)^4$ in a model which correlated the empirical temperature variation of the penetration depth $\lambda^{-2} \sim [1 - (T/T_c)^4]$ with a similar variation of n_s/n in the London theory. As indicated by the dashed curve in Fig. 3.8, this gives a qualitative fit to the ultrasonic-attenuation result; but it cannot possibly explain the rise in $1/T_{1s}$ above $1/T_{1n}$ since that would require the number of normal electrons to exceed the total number of electrons, despite the existence of “superconducting electrons” as well.

Let us now examine this in more detail. We are again interested in the limit in which $\hbar\omega = \hbar\gamma H$ is much less than Δ and kT . However, we cannot proceed as simply as before because for the case II coherence factors $\alpha_s/\alpha_n \rightarrow \infty$ as $\omega \rightarrow 0$. However, we can still simplify the Fermi function by converting to a derivative form. Thus,

$$\frac{\alpha_s}{\alpha_n} = 2 \int_{\Delta}^{\infty} \frac{E(E + \hbar\omega) + \Delta^2}{(E^2 - \Delta^2)^{1/2}[(E + \hbar\omega)^2 - \Delta^2]^{1/2}} \left(-\frac{\partial f}{\partial E} \right) dE \quad (3.93)$$

where the factor of 2 results from the fact that the integration over negative energies $(E + \hbar\omega) \leq -\Delta$ gives exactly the same contribution as the integration over positive energies $E \geq \Delta$. If we now try to set $\omega = 0$, we find

$$\frac{\alpha_s}{\alpha_n} = 2 \int_{\Delta}^{\infty} \frac{E^2 + \Delta^2}{E^2 - \Delta^2} \left(-\frac{\partial f}{\partial E} \right) dE$$

which is easily seen to diverge logarithmically from the integration at Δ . If one kept ω finite, the divergence would be replaced by a factor of order $\ln(\Delta/\hbar\omega) \sim 10$ for typical values. This is still much greater than the experimentally observed rise in $1/T_1$, typically only a factor of 2, before the exponential fall at low temperatures. Thus, some other concept must be brought in to explain this quantitative discrepancy. The origin of the incipient divergence in α_s can be traced to the product of the two highly peaked, superconducting density-of-states factors in (3.93). Dropping nonsingular factors, we obtain

$$\alpha \propto \int N(E)N(E + \hbar\omega)dE \approx \int N^2(E) dE$$

for $\hbar\omega \ll \Delta$. Since $\int N(E) dE$ is conserved on going into the superconducting state, the sharp rise of $N_s(E)$ must cause $\int N_s^2 dE$ to exceed $\int N_n^2 dE$. An excessively high value of α results if we have overestimated the sharpness of the peak in state density by using the simple BCS form.

Two reasons have been advanced for the apparent extra breadth in the peak in the density of states. The first is that the anisotropy of the energy gap in real crystals leads to a range in $\Delta_{\mathbf{k}}$ over the Fermi surface. Thus, the peaks in $N_s(E)$ will be smeared out over a fractional energy range, typically $\frac{1}{10}$. Experiments of

Masuda⁴¹ on aluminum with varying amounts of impurity support this explanation. He observed a bigger rise of $1/T_1$ in the dirtier samples. This is consistent with the Anderson theory of dirty superconductors, which holds that the gap should become more nearly the same for all electrons when rapid electron scattering causes electrons to sample many \mathbf{k} values during the relevant time interval \hbar/Δ .

The other explanation, due to Fibich,⁴² is that the finite lifetime of the quasi-particle states against decay into phonons limits the sharpness of the peak, as indicated by an uncertainty-principle argument. Such a mechanism would be expected to be roughly independent of impurity but more important in strong-coupling superconductors. Some data on indium seem to support this mechanism. Thus, both mechanisms seem important in appropriate situations.

We conclude this section by noting that the high-temperature superconductors seem to show *no* Hebel-Slichter peak at all. As discussed in Sec. 9.9, this may reflect a gapless density of states associated with nonconventional pairing.

3.9.3 Electromagnetic Absorption

Since the interaction hamiltonian $\mathbf{p} \cdot \mathbf{A}$ also obeys the case II coherence factors, we can carry over the results of the previous section on nuclear relaxation without modification to describe the absorption of low-frequency electromagnetic radiation. The quantity α_s/α_n is now called σ_{1s}/σ_n since for a given E field the electromagnetic energy absorption per unit volume is $\sigma_1 E^2$, where σ_1 is the real part of the complex conductivity $\sigma_1(\omega) - i\sigma_2(\omega)$. Thus, for $\hbar\omega \ll \Delta$, we expect σ_{1s}/σ_n to rise above unity just below T_c and then to fall exponentially to zero at low temperatures. As noted earlier, such behavior is qualitatively incompatible with a simple two-fluid picture in which $n_n \leq n$.

Unlike the case of nuclear relaxation, however, it is now possible to utilize frequencies large enough to create pairs of quasi-particles. Such processes occur, in addition to the scattering processes treated already, as soon as $\hbar\omega \geq 2\Delta$. In fact, at $T = 0$, there are no thermally excited quasi-particles present, and the *only* process allowing absorption of energy is the creation of pairs. With our semiconductor sign conventions, the initial state energy E must be $\leq -\Delta$, and the final state energy $E + \hbar\omega \geq \Delta$. Thus, $\sigma_1(\omega) = 0$ for $\hbar\omega < 2\Delta$, at which point there is an *absorption edge*, as shown in Fig. 3.10. The absorption can be computed by using (3.91), with the Fermi functions being either 0 or 1 at $T = 0$. Thus,

$$\left. \frac{\sigma_{1s}}{\sigma_n} \right|_{T=0} = \frac{1}{\hbar\omega} \int_{\Delta-\hbar\omega}^{-\Delta} \frac{|E(E+\hbar\omega) + \Delta^2|}{(E^2 - \Delta^2)^{1/2} [(E+\hbar\omega)^2 - \Delta^2]^{1/2}} dE \quad (3.94)$$

⁴¹Y. Masuda, *Phys. Rev.* **126**, 1271 (1962).

⁴²M. Fibich, *Phys. Rev. Lett.* **14**, 561 (1965).

As shown by Mattis and Bardeen,⁴³ this integral can be expressed in terms of the tabulated complete elliptic integrals E and K , namely,

$$\frac{\sigma_{1s}}{\sigma_n} \Big|_{T=0} = \left(1 + \frac{2\Delta}{\hbar\omega} \right) E(k) - \frac{4\Delta}{\hbar\omega} K(k) \quad \hbar\omega \geq 2\Delta \quad (3.95)$$

where

$$k = \frac{\hbar\omega - 2\Delta}{\hbar\omega + 2\Delta} \quad (3.95a)$$

As shown in Fig. 3.10, σ_{1s}/σ_n rises from zero with finite slope at $\hbar\omega = 2\Delta$ and slowly approaches unity for $\hbar\omega \gg 2\Delta$. At finite temperatures, $\Delta(T) < \Delta(0)$, and also the thermally excited quasi-particles contribute absorption for $\hbar\omega < 2\Delta(T)$. Numerical calculations are needed to describe the exact behavior, but the qualitative behavior for $T > 0$ is indicated by the dashed curve. The rise as $\hbar\omega \rightarrow 0$ is the logarithmic dependence discussed in connection with $1/T_1$.

Historically speaking, the first spectroscopic measurements clearly showing the existence and width of the energy gap in superconductors well below T_c were made by Glover and Tinkham⁴⁴ with far-infrared radiation in the region of the absorption edge. These first measurements slightly preceded the appearance of the BCS theory but were soon found to be in excellent accord with (3.95). With improvements in techniques over the years,⁴⁵ the quality of data has reached the state that small deviations from the simple BCS curves observed in measure-

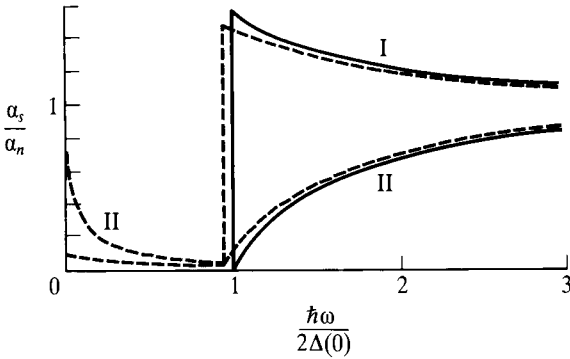


FIGURE 3.10

Frequency dependence of absorption processes obeying case I and II coherence factors at $T = 0$ (solid curves) and $T \approx \frac{1}{2} T_c$ (dashed curves).

⁴³D. C. Mattis and J. Bardeen, *Phys. Rev.* **111**, 412 (1958).

⁴⁴R. E. Glover and M. Tinkham, *Phys. Rev.* **104**, 844 (1956).

⁴⁵D. M. Ginsberg and M. Tinkham, *Phys. Rev.* **118**, 990 (1960); L. H. Palmer and M. Tinkham, *Phys. Rev.* **165**, 588 (1968).

ments on thin lead films can be interpreted in terms of strong-coupling effects analogous to the phonon structure observed in tunneling experiments.

It is worth remarking that with case I coherence factors, α_s/α_n rises discontinuously at $\hbar\omega = 2\Delta$ to a value greater than 1, and then decreases, as shown in Fig. 3.10. One can show that the total area under the curve is conserved in this case, whereas for case II the area seems to disappear when the gap opens up. However, the oscillator-strength sum rule in the form⁴⁶

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\pi n e^2}{2m}$$

requires that the area under the curve of $\sigma_1(\omega)$ have the same value in the superconducting as in the normal state. Tinkham and Ferrell⁴⁷ were able to argue that the "missing area" A at finite frequencies appears as a δ function at $\omega = 0$, which physically represents the absorption of energy from a dc electric field to supply the kinetic energy of the accelerated supercurrent. The argument is based on the Kramers-Kronig relations,⁴⁸ which connect the real and imaginary parts of any causal linear-response function. Written in terms of the complex conductivity $\sigma_1 - i\sigma_2$, and with a time dependence of $e^{+i\omega t}$, they have the form

$$\sigma_1(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \sigma_2(\omega') d\omega'}{\omega'^2 - \omega^2} + \text{const} \quad (3.96a)$$

$$\sigma_2(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\sigma_1(\omega') d\omega'}{\omega'^2 - \omega^2} \quad (3.96b)$$

From (3.96b) we see that a term $\sigma_1 = A \delta(\omega)$ yields $\sigma_2 = 2A/\pi\omega$. For comparison, the London equation (1.3) is equivalent to $\sigma_2 = 1/\Lambda\omega = n_s e^2/m\omega = c^2/4\pi\lambda^2\omega$. Thus, we see that the penetration depth is related to the missing area by $\lambda^{-2} = 8A/c^2$, so that in principle the dc superconducting properties can be computed from the high-frequency absorption spectrum. Roughly speaking, the gap implies the superconductivity, but more carefully, it is the missing area that is important. The example of case I coherence factors, mentioned earlier, shows that the missing area is not a necessary consequence of the energy gap; case II coherence factors are also required. Thus, the coherence factors are a more essential feature of superconductivity than is the gap in the spectrum. This point is driven home by recalling that *semiconductors* have gaps but are not superconducting (because there is no missing area), whereas it has been shown that superconduc-

⁴⁶See, e.g., R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).

⁴⁷M. Tinkham and R. A. Ferrell, *Phys. Rev. Lett.* **2**, 331 (1959).

⁴⁸For a more detailed discussion of the application of sum rule and Kramers-Kronig methods to superconducting electrodynamics, see the chapter on superconductivity by M. Tinkham in C. de Witt, B. Dreyfus, and P. G. de Gennes (eds.), *Low Temperature Physics*, Gordon and Breach, New York (1962). Also, see Sec. 2.5.1 of this book.

tors made gapless by magnetic impurities retain superconducting properties as long as there is still a missing area under the $\sigma_1(\omega)$ curve.

3.10 ELECTRODYNAMICS

The simple treatment just given of the absorption of electromagnetic fields gives no direct account of the dramatic supercurrent properties because we restricted our discussion to dissipative processes analogous to those of normal electrons. Rather than undertake the complications of a complete treatment of the response of a superconductor to an arbitrary electromagnetic field, we shall content ourselves with a treatment of the response to a static magnetic field. This response must be nondissipative, and hence is complementary to that just treated. Since the Meissner effect and related superfluid responses are nearly independent of frequency until one reaches frequencies on the order of the gap, this treatment actually is useful in a wide range of applications.

In the cases of interest, the field can be described by a classical transverse vector potential $\mathbf{A}(\mathbf{r})$ such that $\mathbf{B} = \text{curl } \mathbf{A}$. These are the total fields, including the effects of screening by supercurrents, which will have to be introduced in a self-consistent way. In the presence of a vector potential, it is well known that the canonical momentum of both classical and quantum mechanics contains a potential-momentum term as well as the usual kinetic momentum, so that $\mathbf{p} = m\mathbf{v} + e\mathbf{A}/c$, where e is the charge of the particle. The kinetic energy $\frac{1}{2}mv^2$ then becomes $(\mathbf{p} - e\mathbf{A}/c)^2/2m$, whereas the potential-energy expression is unchanged. Since we are interested only in calculating the linear response to weak fields, we can expand this kinetic-energy expression, keeping only terms linear in \mathbf{A} . With the operator replacement $\mathbf{p}_i \rightarrow -i\hbar\nabla_i$, the resulting perturbation term is

$$\mathcal{H}_1 = \frac{ie\hbar}{2mc} \sum_i (\nabla_i \cdot \mathbf{A} + \mathbf{A} \cdot \nabla_i)$$

where the sum runs over all the particles. If the vector potential is expanded in spatial Fourier components

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{a}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}$$

\mathcal{H}_1 may be written

$$\mathcal{H}_1 = -\frac{e\hbar}{mc} \sum_{\mathbf{k}, \mathbf{q}} \mathbf{k} \cdot \mathbf{a}(\mathbf{q}) c_{\mathbf{k}+\mathbf{q}, \sigma}^* c_{\mathbf{k}, \sigma} \quad (3.97)$$

since $\mathbf{q} \cdot \mathbf{a}(\mathbf{q}) = 0$ for a transverse field, by definition. Because the dominant interaction is with the orbital motion, the spin index is unchanged. The explicit form of the $\mathbf{B}_{\mathbf{k}'\sigma', \mathbf{k}\sigma}$ of (3.84) may be read out from (3.97). From the proportionality of

these matrix elements to \mathbf{k} we see that they are of case II, as noted earlier, and following (3.87), the interaction can be written out in full as

$$\begin{aligned} \mathcal{H}_1 = & -\frac{e\hbar}{mc} \sum_{\mathbf{k}, \mathbf{q}} \mathbf{k} \cdot \mathbf{a}(\mathbf{q}) [u_{\mathbf{k}} u_{\mathbf{k}+\mathbf{q}} + v_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}}] (\gamma_{\mathbf{k}+\mathbf{q}, 0}^* \gamma_{\mathbf{k}, 0} - \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}+\mathbf{q}, 1}) \\ & + (v_{\mathbf{k}} u_{\mathbf{k}+\mathbf{q}} - u_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}}) (\gamma_{\mathbf{k}+\mathbf{q}, 0}^* \gamma_{\mathbf{k}1}^* - \gamma_{\mathbf{k}+\mathbf{q}, 1} \gamma_{\mathbf{k}0}) \end{aligned} \quad (3.98)$$

In the preceding section, we dealt with the energy absorption due to this operator. Now we consider the *current* induced by this perturbation. In the presence of a vector potential, the current consists of two terms, \mathbf{J}_1 and \mathbf{J}_2 , corresponding to the two terms in $\mathbf{v} = (\mathbf{p}/m) - (e\mathbf{A}/mc)$. The second term gives the simple result

$$\mathbf{J}_2 = -\frac{ne^2}{mc} \mathbf{A} \quad (3.99)$$

which would correspond exactly to the London equation (1.8) if n could be interpreted as n_s , the number of "superconducting electrons." In fact, though, n is always the *total* electron density, and this term has the same value also in the normal state. Thus, the first term \mathbf{J}_1 , often called the *paramagnetic* current term because it tends to cancel the diamagnetic current \mathbf{J}_2 , must play a vital role. It is not hard to see that the \mathbf{q} th Fourier component of \mathbf{J}_1 will be found by evaluating the operator

$$\mathbf{J}_1(\mathbf{q}) = \frac{e\hbar}{m} \sum_{\mathbf{k}} \mathbf{k} c_{\mathbf{k}-\mathbf{q}}^* c_{\mathbf{k}} \quad (3.100)$$

which may then be expanded in terms of the γ operators to give a form analogous to (3.98).

Before proceeding with detailed calculations, it is convenient to introduce a standard notation for describing the current response to the various Fourier components of a vector potential, namely,

$$\mathbf{J}(\mathbf{q}) = -\frac{c}{4\pi} K(\mathbf{q}) \mathbf{a}(\mathbf{q}) \quad (3.101)$$

For example, in the London theory, where

$$\mathbf{J}(\mathbf{r}) = -\frac{1}{c\Lambda} \mathbf{A}(\mathbf{r}) = -\frac{c}{4\pi\lambda^2} \mathbf{A}(\mathbf{r}) \quad (3.102)$$

the response is independent of \mathbf{q} , and

$$K(\mathbf{q}) = K(0) = \frac{1}{\lambda^2} \quad (3.103)$$

Using the definition $\lambda_L^2(0) = mc^2/4\pi ne^2$ for the ideal limit at $T = 0$ and (3.99), we may write the response function, including both \mathbf{J}_1 and \mathbf{J}_2 , as

$$K(\mathbf{q}, T) = \lambda_L^{-2}(0) [1 + \lambda_L^2(0) K_1(\mathbf{q}, T)] \quad (3.104)$$

where the preceding discussion leads us to expect that K_1 will be negative. As we are restricting our attention to isotropic systems and transverse fields, $K(\mathbf{q})$ is a function only of $|\mathbf{q}|$, and we shall normally denote it simply $K(q)$.

It is also useful to consider, in general, the relation between a q -dependent $K(q)$ and the corresponding nonlocal response in coordinate space described by a range function or kernel $F(R)$ in the expression

$$\mathbf{J}(\mathbf{r}) = C \int \frac{\mathbf{R}[\mathbf{R} \cdot \mathbf{A}(\mathbf{r}')]]}{R^4} F(R) d\mathbf{r}' \quad (3.105)$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. By inserting $\mathbf{A}(\mathbf{r}') \sim e^{i\mathbf{q} \cdot \mathbf{r}'}$, one can show that the relation between $K(q)$ and $F(R)$ is

$$K(q) = \frac{16\pi^2 C}{3c} \int_0^\infty \left[\frac{3}{qR} j_1(qR) \right] F(R) dR \quad (3.106)$$

where $j_1(x) = x^{-2} \sin x - x^{-1} \cos x$ is a spherical Bessel function, such that $[3x^{-1}j_1(x)]$ is a damped oscillatory function with the value unity for $x = 0$. Thus,

$$K(0) = \frac{16\pi^2 C}{3c} \int_0^\infty F(R) dR \quad (3.106a)$$

depends on the integral of $F(R)$, whereas as $q \rightarrow \infty$

$$K(q) \xrightarrow{q \rightarrow \infty} \frac{16\pi^2 C}{3c} \frac{F(0)}{q} \int_0^\infty \frac{3}{x} j_1(x) dx = \frac{4\pi^3 C F(0)}{cq} \quad (3.106b)$$

which depends only on the value of $F(R)$ at the origin. Taking the ratio, we have

$$\frac{K(q)}{K(0)} \xrightarrow{q \rightarrow \infty} \frac{3\pi}{4qL} \quad (3.106c)$$

where $L = F^{-1}(0) \int F(R) dR$ is a measure of the range of the real-space kernel $F(R)$. These relations are very general; they apply to the relation between \mathbf{J} and \mathbf{E} in the normal state with $L = \ell$ and to the relation between \mathbf{J} and \mathbf{A} in the superconducting state with, as we shall soon see, $L \approx \xi_0$.

3.10.1 Calculation of $K(0, T)$ or $\lambda_L(T)$

Now let us proceed to calculate the temperature dependence of $K(q, T)$ for the simple limiting case $q = 0$, which corresponds to infinite wavelength. This will determine the temperature dependence of $\lambda_L(T)$, which is defined (for $\ell = \infty$) by

$$K(0, T) \equiv \frac{1}{\lambda_L^2(T)} \quad (3.107)$$

since the nonlocal theory reduces to the local London theory for fields which vary slowly in space. In other words, the temperature dependence of $K(0, T)$ is identified with the temperature dependence of n_s in the London theory. For $\mathbf{q} = 0$,

obviously the coherence factor in the second term in (3.98) is zero, whereas that in the first term is unity. Moreover, for $\mathbf{q} = 0$, $\gamma_{\mathbf{k}+\mathbf{q}, 0}^* \gamma_{\mathbf{k}0}$ becomes the number operator $\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0}$. Thus, the perturbing hamiltonian (3.98) simply shifts the energies of the quasi-particle excitations, as follows:

$$\begin{aligned} E_{\mathbf{k}0} &\rightarrow E_{\mathbf{k}0} - \frac{e\hbar}{mc} \mathbf{k} \cdot \mathbf{a}(0) \\ E_{\mathbf{k}1} &\rightarrow E_{\mathbf{k}1} + \frac{e\hbar}{mc} \mathbf{k} \cdot \mathbf{a}(0) \end{aligned} \quad (3.108)$$

Similarly, the expansion of $\mathbf{J}_1(0)$ in quasi-particle operators reduces simply to

$$\begin{aligned} \mathbf{J}_1(0) &= \frac{e\hbar}{m} \sum_{\mathbf{k}} \mathbf{k} (\gamma_{\mathbf{k}0}^* \gamma_{\mathbf{k}0} - \gamma_{\mathbf{k}1}^* \gamma_{\mathbf{k}1}) \\ &= \frac{e\hbar}{m} \sum_{\mathbf{k}} \mathbf{k} (f_{\mathbf{k}0} - f_{\mathbf{k}1}) \end{aligned} \quad (3.109)$$

where in the second line the operators have been replaced by their expectation values $f_{\mathbf{k}0}$ and $f_{\mathbf{k}1}$, the Fermi functions corresponding to the shifted energies (3.108). In the limit of small $\mathbf{a}(0)$, $f_{\mathbf{k}0} \approx f_{\mathbf{k}1}$, and the difference may be found by taking the first term in a Taylor's series expansion; i.e.,

$$f_{\mathbf{k}0} - f_{\mathbf{k}1} \approx \left(-\frac{\partial f}{\partial E_{\mathbf{k}}} \right) \frac{2e\hbar}{mc} \mathbf{k} \cdot \mathbf{a}(0)$$

Inserting this in (3.109), we have

$$\mathbf{J}_1(0) = \frac{2e^2\hbar^2}{m^2c} \sum_{\mathbf{k}} [\mathbf{a}(0) \cdot \mathbf{k}] \mathbf{k} \left(-\frac{\partial f}{\partial E_{\mathbf{k}}} \right) \quad (3.110)$$

By symmetry, $\mathbf{J}_1(0)$ is parallel to $\mathbf{a}(0)$, and the average of the square of the component of \mathbf{k} along \mathbf{J}_1 (or \mathbf{a}) will be $k_F^2/3$ since $\cos^2 \theta$ averages to one third over a sphere. Thus, the K_1 corresponding to (3.110) can be written as

$$K_1(0, T) = \frac{-4\pi\mathbf{J}_1(0)}{c\mathbf{a}(0)} = -\left(\frac{4\pi ne^2}{mc^2} \right) \left(\frac{4E_F}{3n} \right) \sum_{\mathbf{k}} \left(-\frac{\partial f}{\partial E_{\mathbf{k}}} \right)$$

Since $N(0) = 3n/4E_F$, this can be rewritten as

$$K_1(0, T) = -\lambda_L^{-2}(0) \int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial E} \right) d\xi$$

Inserting this in (3.104) yields the total response, including \mathbf{J}_1 and \mathbf{J}_2 ,

$$K(0, T) = \lambda_L^{-2}(T) = \lambda_L^{-2}(0) \left[1 - 2 \int_{\Delta}^{\infty} \left(-\frac{\partial f}{\partial E} \right) \frac{E}{(E^2 - \Delta^2)^{1/2}} dE \right] \quad (3.111)$$

We note first that if $\Delta = 0$ (normal state, $T \geq T_c$), then the integral reduces to $f(0) = \frac{1}{2}$, and $K(0, T \geq T_c) = 0$. This corresponds to the absence of any

Meissner effect in the normal state because of the cancellation of the paramagnetic and diamagnetic current terms \mathbf{J}_1 and \mathbf{J}_2 . As soon as $\Delta > 0$, however, the integral no longer gives the exact cancellation, and there is a finite $\lambda_L(T)$ leading to a Meissner effect if the sample is large enough. As T decreases and $\Delta(T)/kT$ increases further, the integral becomes less and less, eventually becoming exponentially small when $\Delta/kT \gg 1$. Thus, $\lambda_L(T)$ defined by (3.111) does reduce properly to $\lambda_L(0)$ as defined by (1.9) when $T \rightarrow 0$, justifying our notations. The general behavior is shown in Fig. 3.11. The physical origin of K_1 is that excitations on the trailing edge of the displaced momentum distribution in \mathbf{k} space have lower energy and thus are more highly populated, so that the excited quasi-particles carry a net current in the reverse direction which partially cancels the current \mathbf{J}_2 . It is conceptually important to recognize that the *total* response, including the (negative) quasi-particle contribution, is the supercurrent. The quasi-particle contribution does not die away because it represents a distribution giving minimum free energy.

In considering Fig. 3.11, we should keep in mind that $\lambda_L(T)$ will give the temperature dependence of the experimentally observed penetration depth only if the strength of the response to the self-consistent vector potential is adequately approximated by the response to the component with $\mathbf{q} = 0$. We now consider the q dependence of $K(q, T)$ to clarify this point.

3.10.2 Calculation of $K(q, 0)$

For simplicity, we shall examine the q dependence only at $T = 0$, although the calculation is readily extended by use of appropriate statistical techniques. At $T = 0$, the electrons must be in the BCS ground state $|\psi_G\rangle$. Then by ordinary first-order perturbation theory, the perturbed state $|\psi\rangle$ in the presence of \mathcal{H}_1 is

$$|\psi\rangle = |\psi_G\rangle - \sum_n \frac{\langle \psi_n | \mathcal{H}_1 | \psi_G \rangle}{E_n} |\psi_n\rangle$$

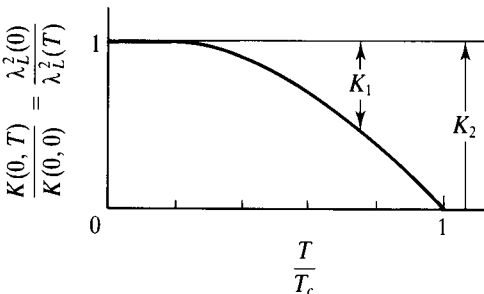


FIGURE 3.11

Temperature dependence of $K(0, T)/K(0, 0) = \lambda_L^2(0)/\lambda_L^2(T) = n_s(T)/n$ according to the BCS theory. Note that $K(0, T)$ is the result of the partial cancellation of the constant diamagnetic term K_2 by the temperature-dependent paramagnetic term K_1 .

where the sum on n runs over the various excited states with excitation energy E_n . Taking the expectation value of $\mathbf{J}_1(\mathbf{q})$ over $|\psi\rangle$, we have

$$\langle\psi|\mathbf{J}_1(\mathbf{q})|\psi\rangle = \langle\psi_G|\mathbf{J}_1(\mathbf{q})|\psi_G\rangle - 2 \operatorname{Re} \sum_n \frac{\langle\psi_G|\mathbf{J}_1(\mathbf{q})|\psi_n\rangle\langle\psi_n|\mathcal{H}_1|\psi_G\rangle}{E_n}$$

The first term is zero since the electrons all have paired momenta. In the second term, the only contribution comes from states ψ_n containing two quasi-particles generated by the term $\gamma_{\mathbf{k}+\mathbf{q},0}^* \gamma_{\mathbf{k}1}^*$ in (3.98). Since the same coherence factor appears in the matrix elements of $\mathbf{J}_1(\mathbf{q})$ as in the elements of \mathcal{H}_1 , we find

$$\langle\psi|\mathbf{J}_1(\mathbf{q})|\psi\rangle = \frac{2e^2\hbar^2}{m^2c} \sum_{\mathbf{k}} \frac{(\nu_{\mathbf{k}}u_{\mathbf{k}+\mathbf{q}} - u_{\mathbf{k}}\nu_{\mathbf{k}+\mathbf{q}})^2}{E_{\mathbf{k}} + E_{\mathbf{k}+\mathbf{q}}} [\mathbf{k} \cdot \mathbf{a}(\mathbf{q})]\mathbf{k} \quad (3.112)$$

This term obviously gives a current parallel to \mathbf{A} , partially canceling the diamagnetic current \mathbf{J}_2 , even at $T = 0$. The amount of cancellation depends on q , going to zero at $q = 0$, as noted earlier.

Using arguments similar to those used to reach (3.111), (3.112) leads to

$$K(q, 0) = \lambda_L^{-2}(0) \left\{ 1 - \int_{-\infty}^{\infty} \frac{(\nu_{\mathbf{k}}u_{\mathbf{k}+\mathbf{q}} - u_{\mathbf{k}}\nu_{\mathbf{k}+\mathbf{q}})^2}{E_{\mathbf{k}} + E_{\mathbf{k}+\mathbf{q}}} d\xi \right\} \quad (3.113)$$

for the response function K . Without going into details, one can see that this implies that as q first increases from zero, $K(q, 0)$ decreases by a fractional amount of the order of $q^2\xi_0^2$, where, following BCS, ξ_0 is defined by

$$\xi_0 \equiv \frac{\hbar v_F}{\pi\Delta(0)} \quad (3.114)$$

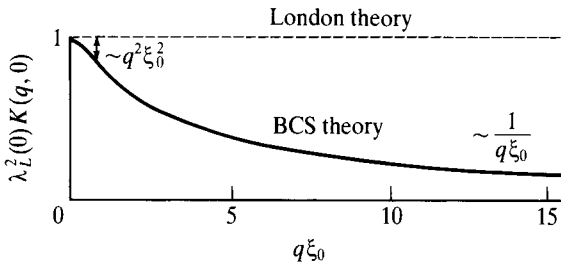
[This follows since the coherence factor in the numerator can be written for small \mathbf{q} as $(\xi_{\mathbf{k}+\mathbf{q}} - \xi_{\mathbf{k}})\partial(u_{\mathbf{k}} - \nu_{\mathbf{k}})/\partial\xi_{\mathbf{k}}$; the first factor is of order $\hbar v_F q$, and the second is of order $1/\Delta(0)$ for the important part of the integration region.] On the other hand, if $q\xi_0 \gg 1$, to a first approximation the integral in (3.113) cancels the first term, leaving a residual value of

$$K(q, 0) = K(0, 0) \frac{3\pi}{4q\xi_0} \quad q\xi_0 \gg 1 \quad (3.115)$$

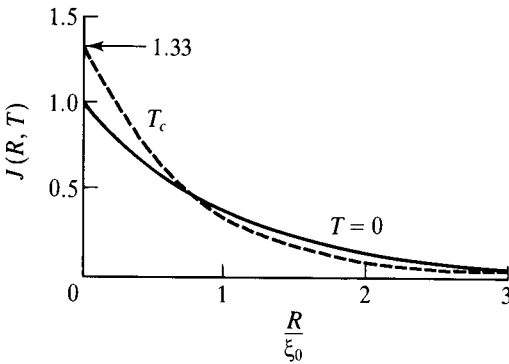
as anticipated in (3.106c). The complete dependence of $K(q, 0)$ on q is shown in Fig. 3.12. Note that the response of the normal state at $T = 0$ can be obtained as the limit $\Delta(0) \rightarrow 0$, which leads to $\xi_0 \rightarrow \infty$, so that $K(q, 0) = 0$ for all q .

3.10.3 Nonlocal Electrodynamics in Coordinate Space

Given $K(q, T)$, one can find the corresponding real-space kernel by Fourier transformation, the inverse of the transformation leading to (3.106). The result, called $J(R, T)$ by BCS, is sketched in Fig. 3.13. It is very similar to the


FIGURE 3.12

Comparison of q -dependent response of the nonlocal BCS theory with the q -independent response of the local London theory. In both cases, the curves are drawn for pure metals, with infinite mean free paths.


FIGURE 3.13

Schematic comparison of the BCS range function $J(R, T)$ at $T=0$ and T_c . Note that the range of nonlocality is reduced by a factor of about 0.75 on going from $T=0$ to T_c .

exponential form e^{-R/ξ_0} proposed by Pippard.⁴⁹ In fact, the $J(R, T)$ of BCS is normalized so that

$$\int_0^\infty J(R, T) dR = \xi_0 = \int_0^\infty e^{-r/\xi_0} dR \quad (3.116)$$

with ξ_0 as defined in (3.114). At $R=0$, the value of J ranges smoothly from 1 at $T=0$ to 1.33 at $T=T_c$, whereas in the Pippard approximation, the value of the exponential kernel at $R=0$ remains unity at all temperatures. Apart from this minor difference, the similarity is remarkably complete.

⁴⁹A. B. Pippard, *Proc. Roy. Soc. (London)* **A216**, 547 (1953).

Inserting the normalization (3.115) into (3.106a) and recalling the definition (3.107), we see that the BCS version of the nonlocal current relation (3.105) becomes

$$\mathbf{J}(\mathbf{r}) = -\frac{3c}{16\pi^2\xi_0\lambda_L^2(T)} \int \frac{\mathbf{R}[\mathbf{R} \cdot \mathbf{A}(\mathbf{r}')]]}{R^4} J(R, T) d\mathbf{r}' \quad (3.117)$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. This differs from the Pippard form (1.11) only by the substitution of $J(R, T)$ for the exponential e^{-R/ξ_0} . If $\mathbf{A}(\mathbf{r}')$ is constant over the range of $J(R, T)$, (3.117) reduces to the London relation

$$\mathbf{J}(\mathbf{r}) = -\frac{c}{4\pi\lambda_L^2(T)} \mathbf{A}(\mathbf{r}) \quad (3.118)$$

However, if $\mathbf{A}(\mathbf{r})$ is varying significantly on the scale of ξ_0 , this reduction cannot be made, and the nonlocality of the electrodynamics must be taken into account.

3.10.4 Effect of Impurities

Our results so far have been for the case of a pure metal, in which \mathbf{k} is a good quantum number, allowing the simple formulation of the BCS pairing theory which we have given. Although generalization of the microscopic theory to include the effects of impurity scattering can be done by Green function techniques, we shall use instead a more phenomenological approach. By analogy with the corresponding expression of Chambers for the nonlocal response of normal electrons to an electric field, we expect a factor of $e^{-R/\ell}$ to multiply the kernel $J(R, T)$, where ℓ is the mean free path. This has the effect of making the electrodynamic response more local, and if ℓ is sufficiently small on the scale of spatial variation of \mathbf{A} , we can always simplify to a local response of the London type (3.118), but with a modified (reduced) coefficient characterized by a $\lambda_{\text{eff}} (> \lambda_L)$. The appropriate value of λ_{eff} is determined by

$$\frac{\lambda_L^2(T)}{\lambda_{\text{eff}}^2(\ell, T)} = \frac{K(0, T, \ell)}{K(0, T, \infty)} = \frac{\int_0^\infty J(R, T) e^{-R/\ell} dR}{\xi_0} \quad (3.119)$$

where we have used (3.106a) and (3.116). [Note that we restrict use of the notation $\lambda_L(T)$ to characterize the response of *pure* metal at $q = 0$].

To avoid numerical evaluation of (3.119), we first consider the *extreme dirty limit*, $\ell \ll \xi_0$, in which the integral in the numerator reduces simply to $J(0, T)\ell$. Then

$$\lambda_{\text{eff}}(\ell, T) = \lambda_L(T) \left(\frac{\xi_0}{\ell} \right)^{1/2} [J(0, T)]^{-1/2} \quad (3.120)$$

Since $J(0, T)$ ranges only from 1 at $T = 0$ to 1.33 at T_c , the final factor introduces only a small correction.

Another convenient approximation is to use the Pippard exponential e^{-R/ξ_0} for $J(R, T)$. If this is done, the integral in (3.119) becomes simply ξ , where

$$\xi^{-1} = \xi_0^{-1} + \ell^{-1} \quad (3.121)$$

and then
$$\lambda_{\text{eff}}(\ell, T) = \lambda_L(T) \left(\frac{\xi_0}{\xi} \right)^{1/2} = \lambda_L(T) \left(1 + \frac{\xi_0}{\ell} \right)^{1/2} \quad (3.122)$$

This approximation is useful even when ℓ is not very small since it reduces to λ_L in the pure limit, and as a result, it has been commonly used. However, the approximation is inexact in that it is missing the factor $[J(0, T)]^{-1/2}$ of the microscopic theory in the dirty limit (3.120).

This defect can be remedied by a simple improvement. We retain the exponential approximation for the form of $J(R, T)$, but we replace e^{-R/ξ_0} by $J(0, T) \exp -[J(0, T)R/\xi_0]$. This new form agrees with the microscopic $J(R, T)$ in its initial value at $R = 0$ as well as in its integral over R . With this improvement, (3.122) is replaced by

$$\lambda_{\text{eff}}(\ell, T) = \lambda_L(T) \left(\frac{\xi'_0}{\xi'} \right)^{1/2} = \lambda_L(T) \left(1 + \frac{\xi'_0}{\ell} \right)^{1/2} \quad (3.123)$$

where the modified Pippard coherence lengths ξ' and ξ'_0 are defined by the relation

$$\frac{1}{\xi'} \equiv \frac{1}{\xi'_0} + \frac{1}{\ell} \equiv \frac{J(0, T)}{\xi_0} + \frac{1}{\ell} \quad (3.123a)$$

Clearly, (3.123) reduces properly to (3.120), but also behaves well when ℓ is not small. Thus, (3.123) gives a very good approximation for the $q \approx 0$ response over the entire range of its arguments. It will also give a good approximation to the actual penetration depth if $\xi \ll \lambda_{\text{eff}}$, where ξ is given by (3.121). Note that (3.123) reduces to (3.122) at $T = 0$ and to

$$\lambda_{\text{eff}}(\ell, T) = \lambda_L(T) \left(1 + 0.75 \frac{\xi_0}{\ell} \right)^{1/2} \quad (3.123b)$$

for $T \approx T_c$. The latter form is often used in connection with the Ginzburg-Landau theory, which is valid near T_c .

3.10.5 Complex Conductivity

The discussion of the complex conductivity $\sigma(\omega)$ in a two-fluid approximation in Sec. 2.5.1 is restricted to frequencies well below the energy-gap frequency ω_g . In the present section, we take up the complementary regime that occurs when ω is of the same order as ω_g .

In the section on transition probabilities and absorption, we worked out an expression [(3.91) with the upper sign] for the ratio of the real part of the complex conductivity in the superconducting state to that of the normal state, σ_{1s}/σ_n , as a function of frequency. Now that we have worked out the low-frequency lossless

response to a vector potential, we can embed the conductivity result in a more general picture. Since we can write

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\frac{i\omega \mathbf{A}}{c}$$

for a periodic electromagnetic field, we can define a complex conductivity proportional to $K(q, \omega, T)$. Equating two expressions for the current

$$\mathbf{J}(q, \omega, T) = \sigma(q, \omega, T) \mathbf{E}(q, \omega) = -\frac{c}{4\pi} K(q, \omega, T) \mathbf{A}(q, \omega)$$

we have

$$\sigma(q, \omega, T) = \frac{ic^2}{4\pi\omega} K(q, \omega, T) \quad (3.124)$$

Of course, we have worked out only some special cases of $K(q, \omega, T)$ [or $\sigma(q, \omega, T)$] in any detail, but these serve to outline much of the general behavior.

A simple analytic form can be given for the temperature variation of the low-frequency limit of σ_2/σ_n , namely,

$$\frac{\sigma_2}{\sigma_n} = \frac{\pi\Delta}{\hbar\omega} \tanh \frac{\Delta}{2kT} \quad \hbar\omega \ll 2\Delta \quad (3.125)$$

which has the limiting forms

$$\frac{\sigma_2}{\sigma_n} \rightarrow \begin{cases} \frac{\pi\Delta}{\hbar\omega} & T \ll T_c \\ \frac{\pi}{2} \frac{\Delta^2}{kT\hbar\omega} & T \approx T_c \end{cases} \quad (3.125a)$$

$$(3.125b)$$

Relating these expressions to the London theory, in which

$$\sigma_{2L} = \frac{n_s e^2}{m\omega} \quad (3.126)$$

we see that these results correspond to $n_s \sim \Delta$ for $T \ll T_c$, but to $n_s \sim \Delta^2$ for $T \approx T_c$. Given Gor'kov's demonstration that near T_c the phenomenological ψ function of the Ginzburg-Landau (GL) theory is proportional to the gap Δ in the BCS theory, the latter result corresponds to the central identification of $n_s \sim |\psi|^2$ in the GL theory, which we discuss in the next chapter.

In terms of our present, more complete picture of a nonlocal or q -dependent response, we must ask: What is the region of validity of the expression for σ_{1s}/σ_n as given by (3.91) or (3.95)? It turns out that these expressions are valid when the response is determined by the value of the nonlocal response kernel for $R = 0$. This will be the case in the dirty limit, $\ell \ll \xi_0$, where the factor $e^{-R/\ell}$ cuts off before $J(R, \omega, T)$ changes very much. It will also be the case when $q\xi_0 \gg 1$, the *extreme anomalous limit* since in this case the appropriate Fourier transform (3.106b) gives weight mainly to a region extending only to about π/q from the origin. In both these limits, σ_n is real, so that $\sigma_n = \sigma_{1n}$. In the dirty limit, both σ_s and σ_n are proportional to ℓ ; in the extreme anomalous limit, both are propor-

tional to $1/q$. Thus, in both limits, the ratio σ_s/σ_n is dependent only on ω and T , permitting us to drop q and ℓ from the notation so long as we remember the limitation to $q\xi_0 \gg 1$ or $\ell \ll \xi_0$.

An explicit form for σ_2 at $T = 0$ analogous to (3.95) for σ_1 can be worked out, namely,

$$\frac{\sigma_{2s}}{\sigma_n} = \frac{1}{2} \left(1 + \frac{2\Delta}{\hbar\omega} \right) E(k') - \frac{1}{2} \left(1 - \frac{2\Delta}{\hbar\omega} \right) K(k') \quad (3.127)$$

where $k' = (1 - k^2)^{1/2}$ and $k = |(2\Delta - \hbar\omega)/(2\Delta + \hbar\omega)|$. The frequency dependence of this function is sketched in Fig. 3.14. Of particular importance is the proportionality of σ_2 to $1/\omega$ for $\hbar\omega \ll 2\Delta$. This corresponds to the fact that $K(q, \omega)$ is essentially independent of frequency there, as required for a frequency-independent penetration depth. More simply, this dependence is a consequence of the free-acceleration aspect of the supercurrent response as described by the London equation $\mathbf{E} = \partial(\Lambda \mathbf{J}_s)/\partial t$. For $\hbar\omega \gtrsim 2\Delta$, σ_2 falls to zero more rapidly than $1/\omega$, but at $\hbar\omega = 2\Delta$, $K(q, \omega)$ has decreased by only a factor of $2/\pi$ from its dc value. Thus, the superfluid response is essentially independent of frequency until microwave frequencies are reached.

The real and imaginary parts of σ both enter into the determination of the response of a superconducting system to time-dependent electromagnetic fields. For example, in the transmission experiments with very thin films, cited earlier in Sec. 3.9, the fractional transmissivity is readily shown to be

$$T = \left[\left(1 + \frac{\sigma_1 d Z_0}{n+1} \right)^2 + \left(\frac{\sigma_2 d Z_0}{n+1} \right)^2 \right]^{-1} \quad (3.128)$$

where n is the index of refraction of the substrate, Z_0 (377 Ω per square in mks units) is the impedance of free space, and d is the film thickness. From (3.128) we see that $T_s \rightarrow 0$ as $\omega \rightarrow 0$ since $\sigma_{2s} \sim 1/\omega \rightarrow \infty$, leading to complete reflection. On the other hand, for $\hbar\omega \gg 2\Delta$, $\sigma_{2s} \rightarrow 0$ and $\sigma_{1s} \rightarrow \sigma_n$, so that $T_s \rightarrow T_n$. In between,

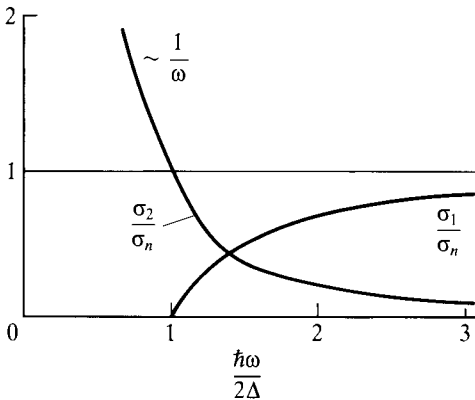


FIGURE 3.14

Complex conductivity of superconductors in extreme anomalous limit (or extreme dirty limit) at $T = 0$. The rise of σ_2 as $1/\omega$ below the gap describes the accelerative supercurrent response. Its coefficient is proportional to the "missing area" under the $\sigma_1(\omega)$ curve at finite frequencies (see the discussion in Sec. 3.9.3).

for $\hbar\omega \approx 2\Delta$, both σ_{1s} and σ_{2s} are smaller than σ_n , as shown in Fig. 3.14, and there is a peak in transmission at which $T_s > T_n$. Observation of these characteristic features by Glover and Tinkham⁵⁰ gave strong support to an energy-gap model of superconductivity and quantitative support to the BCS model in particular.

3.11 THE PENETRATION DEPTH

Having set up the general formalism in the preceding section for treating the electrodynamics of superconductors within the framework of the BCS theory, in this section we apply these results to calculating the predicted magnitude and temperature dependence of the experimentally observed penetration depth λ for a number of important cases. We define λ by the relation

$$\lambda \equiv h(0)^{-1} \int_0^{\infty} h(z) dz \quad (3.129)$$

for penetration into a bulk sample, whether or not the field penetration is exponential. This λ also serves, via (2.2), to determine the parameter n_s of the phenomenological London and GL theories.

To apply the formulas of Sec. 3.10, we need to choose the proper gauge for the vector potential. For the present simple case of a plane surface in a parallel magnetic field, the gauge choice will be uniquely determined by requiring that \mathbf{A} be parallel to the surface but perpendicular to \mathbf{h} and fall off to zero in the interior of the bulk superconductor. On the other hand, in dealing with a thin film in a parallel field of equal strength on both sides, symmetry requires that $|\mathbf{A}|$ pass through zero in the midplane. In other situations, other gauge choices may be required.

3.11.1 Preliminary Estimate of λ for Nonlocal Case

Before going into the rigorous solution for the penetration depth with nonlocal electrodynamics, we first give an elementary argument which yields the form of the results for *Pippard superconductors*, i.e., those with $\xi_0 \gg \lambda_L$.

Even with nonlocal electrodynamics, we expect approximately exponential penetration of the magnetic field, but with a modified penetration depth λ to be determined. If we write $h_y \approx B_0 e^{-z/\lambda}$, where B_0 is the value of the field at the surface, then the form of the vector potential inside the material ($z > 0$) will be $A_x \approx \lambda B_0 e^{-z/\lambda}$ in the appropriate gauge. This can be roughly approximated by the constant value $\bar{A} = \lambda B_0$ over a surface layer of thickness λ and zero elsewhere. In calculating the resulting average current density in the surface layer using the nonlocal form (3.117), we get a value reduced from the London value for this

⁵⁰R. E. Glover and M. Tinkham, *Phys. Rev.* **104**, 844 (1956); **108**, 243 (1957).

average \bar{A} by a factor $\sim \lambda/\xi_0$ since this is the ratio of the volume ($\sim \xi_0^2 \lambda$) in which \bar{A} exists to the effective integration volume ($\sim \xi_0^3$). Thus, we expect

$$\bar{J} \approx -\frac{c}{4\pi\lambda_L^2} \frac{\lambda}{\xi_0} \bar{A} = \frac{c\lambda^2 B_0}{4\pi\lambda_L^2 \xi_0}$$

Applying a Maxwell equation to the surface layer,

$$\frac{B_0}{\lambda} \approx | \langle \text{curl } \mathbf{h} \rangle | = \frac{4\pi\bar{J}}{c} \approx \frac{\lambda^2 B_0}{\lambda_L^2 \xi_0}$$

Solving, we find

$$\lambda \approx (\lambda_L^2 \xi_0)^{1/3} \quad (3.130)$$

with neglect of numerical factors. Thus, when nonlocality is important, i.e., when $\xi_0 \gg \lambda_L$, the actual penetration depth λ will exceed λ_L by a modest factor of order $(\xi_0/\lambda_L)^{1/3}$. If $\xi_0 < \lambda_L$, of course, the preceding argument does not apply because the response is local, and $\lambda \approx \lambda_L$.

Note that (3.130) has a qualitative implication about the temperature dependence of λ in Pippard superconductors. Very near T_c , all superconductors become local since $\lambda_L(T) > \xi_0$, so that $\lambda(T) \approx \lambda_L(T) \sim (T_c - T)^{-1/2}$. At lower temperatures, when $\lambda_L(T) < \xi_0$, it follows from (3.130) that $\lambda(T) \approx (\lambda_L^2 \xi_0)^{1/3} \sim (T_c - T)^{-1/3}$. This implies a crossover of the temperature dependence between the two expressions near the temperature at which $\lambda_L(T) \approx \xi_0$. Since this occurs at different values of T/T_c for different superconductors because of their different values of $\lambda_L(0)/\xi_0$, there cannot be a universal temperature dependence for $\lambda(T)$ in all superconductors. In particular, the famous Gorter-Casimir two-fluid dependence $\lambda(T) = \lambda(0)/[1 - (T/T_c)^4]^{1/2}$ cannot be expected to apply to all materials equally well.

3.11.2 Solution by Fourier Analysis

A convenient technique for obtaining an exact solution to the field penetration problem is to apply Fourier analysis to \mathbf{J} and \mathbf{A} and to use (3.101) to obtain a self-consistent solution. The details of this procedure are given in the appendix. Some care is needed in handling the surface since our expressions from Sec. 3.10 for the response function $\mathbf{K}(q)$ are valid only in an infinite medium. This problem can be handled by the mathematical artifice of introducing externally supplied source currents in the interior of the infinite medium to simulate the field applied at a surface. Different procedures are required for the two limiting cases of completely diffuse and completely specular reflection of electrons at the surface. The results are found to agree for local superconductors and to differ at most by a factor of $\frac{8}{9}$ in the extreme nonlocal limit. This near agreement is fortunate since it is not clear which is the better approximation for the surfaces of real samples. Detailed numerical calculations of the penetration depth in pure

and impure superconductors, with various ratios of $\lambda_L(0)/\xi_0$, have been made by Miller⁵¹ using the exact BCS results for $K(q)$.

In order to avoid these numerical calculations, considerable attention has been given to two limiting cases in which analytic results can be obtained, even though the true situation usually lies in between.

The *local approximation* replaces $K(q)$ for all q by $K(0)$, a constant, thus reducing the problem to the London form, but with a modified penetration depth. Using the generalized Pippard approximation discussed in Sec. 3.10, one finds the results already quoted in (3.123), namely,

$$\lambda_{\text{eff}}(\ell, T) = \lambda_L(T)(1 + \xi'_0/\ell)^{1/2} \quad (3.131)$$

which reduces to $\lambda_{\text{eff}}(\ell, T) = \lambda_L(T)(1 + \xi_0/\ell)^{1/2}$ at $T = 0$ and to $\lambda_{\text{eff}}(\ell, T) = \lambda_L(T)(1 + 0.75\xi_0/\ell)^{1/2}$ near T_c . This approximation is reasonably well justified in dirty superconductors [if $\ell < \lambda(T)$], and even in pure superconductors very near T_c , where $\lambda(T) > \xi_0$. It should also apply to the high-temperature superconductors, provided the BCS model is relevant, because, in them, $\lambda(T) > \xi_0$ at all temperatures and purity levels.

The other approximation is the *extreme anomalous limit*, in which $K(q)$ is replaced at all q values by its asymptotic form for $q \rightarrow \infty$, where $K(q) \sim 1/q$. This should be a reasonable approximation for those pure superconductors with $\lambda_L(0) \ll \xi_0$. For the case of diffuse surface scattering, this calculation yields

$$\lambda_{\infty, \text{diff}} = 0.65(\lambda_L^2 \xi'_0)^{1/3} \quad (3.132)$$

where $\xi'_0 = \xi_0/J(0, T)$ is the modified coherence length based on the BCS electro-dynamics. Since $[J(0, T)]^{1/3}$ varies only from 1 to 1.10 as T ranges from zero to T_c , it is clear that our simple estimate (3.130) captured the essence of this more quantitative result (3.132). For specular surface scattering, the extreme anomalous limit yields the same value as (3.132) times a numerical factor of $\frac{8}{9}$.

Some perspective on the applicability of these results can be gained by consideration of numerical parameters for several pure metals well below T_c . Aluminum is well approximated by λ_{∞} since $\lambda_L \approx 160 \text{ \AA}$, while $\xi_0 \approx 15,000 \text{ \AA}$, so that $\xi_0/\lambda_L \approx 100$. For tin, $\lambda_L \approx 350 \text{ \AA}$, while $\xi_0 \approx 3,000 \text{ \AA}$, so that λ_{∞} is only a moderately good approximation. For lead, $\lambda_L \approx \xi_0/2$, and the London local approximation is actually better than λ_{∞} . In the high T_c materials, one typically has $\lambda_L \approx 1500 \text{ \AA}$ and $\xi_0 \approx 15 \text{ \AA}$, so that the electro-dynamics is completely local, and λ_{∞} is irrelevant. The same is true of typical alloy superconductors, in which the short mean free path assures that $\xi \approx \ell \ll \lambda_L$.

From this survey we see that as a practical matter, the nonlocal electro-dynamics plays a major role only in materials which have high Fermi velocity, low T_c , and a long mean free path, such as clean aluminum. Nonetheless, we have

⁵¹P. B. Miller, *Phys. Rev.* **113**, 1209 (1959).

devoted considerable attention to the subject because of its historical importance in working out the role of the coherence length ξ_0 in explaining why the classic pure superconductors all have measured penetration depths of $\sim 500 \text{ \AA}$, despite having values of λ_L which vary by a factor of 3 from aluminum to lead; this provides a quantitative confirmation of the BCS/Pippard theory.

3.11.3 Temperature Dependence of λ

As noted earlier, $\lambda(T)/\lambda(0)$ cannot have a universal temperature dependence on (T/T_c) in the BCS theory because of the variation of the ratio $\xi_0/\lambda_L(0)$ for different metals. Numerical calculations are required for each case. Yet, the calculated differences are not so great as to be inconsistent with the *approximately* universal “two-fluid” dependence observed experimentally in the classic superconductors, especially since the measurements are often not carried sufficiently near $T = 0$ because of sensitivity limitations. (For high T_c superconductors, the temperature dependence appears to be distinctly different.) To understand this better, let us compare the various predictions with the two-fluid dependence.

The simplest prediction is for a *pure* sample in the *local* limit, where $\lambda(T)/\lambda(0) = \lambda_L(T)/\lambda_L(0)$, whose dependence on T/T_c is given by (3.111). For a pure metal in the extreme *anomalous* limit, (3.132) implies that

$$\frac{\lambda_\infty(T)}{\lambda_\infty(0)} = \left[\frac{\lambda_L^2(T)}{\lambda_L^2(0)J(0, T)} \right]^{1/3} = \left[\frac{\Delta(T)}{\Delta(0)} \tanh \beta\Delta(T)/2 \right]^{-1/3} \quad (3.133)$$

where the second form involves the relation (3.125) and provides a mathematical definition of $J(0, T)$ in terms of $\lambda_L(T)$ and $\Delta(T)$, quantities already defined in (3.111) and (3.53) and included in the numerical tabulation of Mühlshlegel.⁵² Finally, in the *dirty local* limit, (3.131) can be written as

$$\frac{\lambda_{\text{eff}}(T)}{\lambda_{\text{eff}}(0)} = \frac{\lambda_L(T)}{\lambda_L(0)J^{1/2}(0, T)} = \left[\frac{\lambda_\infty(T)}{\lambda_\infty(0)} \right]^{3/2} \quad (3.134)$$

In Fig. 3.15, these various theoretical dependences are compared with the two-fluid approximation

$$\frac{\lambda(T)}{\lambda(0)} = \frac{1}{[1 - (T/T_c)^4]^{1/2}} \quad (3.135)$$

Evidently, the temperature dependence of λ_∞ comes the closest of the theoretical forms to agreement with (3.135). This is satisfying since we expect λ_∞ to be the most appropriate approximation for the typical pure superconductors such as tin, on which the most careful early measurements were made. But, as mentioned previously, the approximation λ_∞ must break down near T_c , when $\lambda(T)$ exceeds

⁵²B. Mühlshlegel, *Z. Phys.* **155**, 313 (1959).

ξ_0 . In particular, the infinite slope of λ_∞^{-2} near T_c would be replaced by the finite slope of λ_L^{-2} in the exact calculation. Note that the difference in zero-temperature normalizations of λ_∞ and λ_L in Fig. 3.15 implies that the slope of λ_L^{-2} near T_c should be increased by a factor $\sim 0.4[\xi_0/\lambda_L(0)]^{2/3}$ before being compared with the slope of the curve for λ_∞^{-2} . Inserting appropriate values in this correction factor brings the slope close to that of the empirical form. In this way, we can see that the full microscopic theory gives a temperature dependence that is closer to the empirical two-fluid law than simply λ_∞ itself. It should also be noticed that Fig. 3.15 implies that a clean, local, weak-coupling BCS superconductor should show a temperature dependence of λ^{-2} which is generally closer to $(1 - t^2)$ than to $(1 - t^4)$, where $t = T/T_c$. Accordingly, the two-fluid temperature dependence should be used only with caution and not assumed to be universal.

3.11.4 Penetration Depth in Thin Films:

λ_{eff} and λ_\perp

The theory of the penetration depth in thin films of nonlocal superconductors has received much attention for several reasons. For one, many of the earlier measurements of $\lambda(T)$ were made intentionally on thin films of thickness $d \sim \lambda$, so that there would be measurable changes in the magnetic moment with changes of T . Accordingly, one needed to ask whether such measured values of λ would be representative of bulk samples. Another reason for interest is that many experiments on superconductors in magnetic fields are performed on thin films, and we

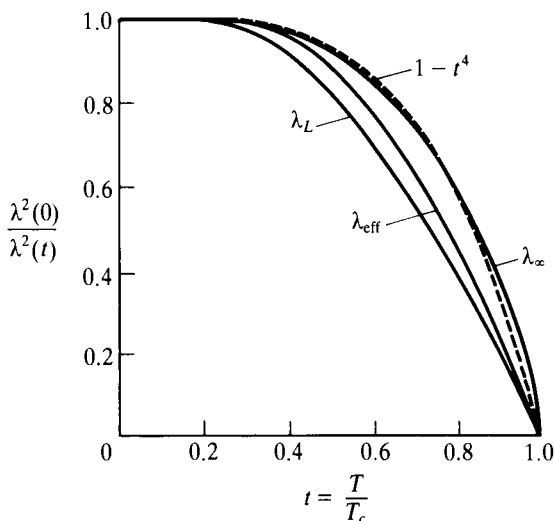


FIGURE 3.15

Comparison of the predicted temperature dependence for $1/\lambda^2$ in various limiting cases of the BCS theory. The dashed curve depicts the empirical approximation (3.135).

wish to understand the interaction between field and film as accurately as possible. Finally, analysis of the behavior of thin films illustrates a further consequence of the nonlocal electrodynamics which does not arise in the basic analysis of the field penetration at the surface of a bulk superconductor.

The end result of this analysis⁵³ is simple. For a sufficiently thin film in *parallel* magnetic field, where we can take the vector potential to have the form $A_y = H_z x$ characteristic of the unscreened field, the supercurrent response of a *nonlocal* superconductor is essentially equivalent to that of a *local* superconductor with

$$\lambda_{\text{eff}} \approx \lambda_L (\xi'_0/d)^{1/2} \quad (\text{for } d \ll \xi'_0) \quad (3.136)$$

with a numerical prefactor estimated to be $\frac{4}{3}$ for diffuse surface scattering and $(\frac{4}{3})^{1/2}$ for specular surface scattering. [Recall that $\xi'_0 = \xi_0/J(0, T)$ was defined in (3.123a).] Note that this result is very similar to (3.131) for the penetration depth of a dirty superconductor with mean free path $\ell \approx d$, the film thickness, as would occur if ℓ were limited by surface scattering.

When a magnetic field is applied *perpendicular* to a thin film ($d \ll \lambda$), quite different considerations enter. In this configuration, the currents serve to control where the flux goes through the film. Accordingly, the vector potential and current density are essentially uniform through the thickness of the film, rather than reversing in direction about the midplane of the film as do the screening currents in the parallel-field case discussed in the previous paragraph. Because \mathbf{A} is uniform through the thickness of the film, the effect of nonlocality on the response depends on the nature of the surface scattering. If it is diffuse, d is the effective thickness over which the uniform \mathbf{A} is integrated in the nonlocal current expression, and λ_{eff} is again given by (3.136) apart from a numerical factor of order unity. On the other hand, if the surface scattering were perfectly specular, the boundary condition implies that a uniform \mathbf{A} should be integrated over all space, and λ_{eff} would be the same as in bulk material of the same purity and mean free path. In practice, (3.136) is usually a reasonable approximation because of a combination of at least partial diffuse surface scattering and an internal mean free path ℓ which is comparable to d .

A much more important consequence of the perpendicular field orientation is that the screening distance λ_{scr} is not given by this λ_{eff} but, rather, by a thickness-dependent $\lambda_{\perp} \approx \lambda^2/d \gg \lambda$, as shown in a classic paper by Pearl.⁵⁴ This λ_{\perp} reflects the effect of the two-dimensional geometry on solutions of Maxwell's equations; it does *not* reflect a change in the intrinsic n_s in the local constitutive relation between \mathbf{J} and \mathbf{A} , which is still described by the λ_{eff} of (3.136). To high-

⁵³See, e.g., M. Tinkham, *Introduction to Superconductivity*, 1st ed., McGraw-Hill, New York (1975), pp. 81–86.

⁵⁴J. Pearl, *Appl. Phys. Lett.* **5**, 65 (1964).

light the centrality of the two- vs. three-dimensional nature of the screening, we now give a heuristic argument which treats both cases in parallel.

We consider the response to an externally imposed filament of current I flowing along a straight line within the superconducting medium and work out the screening length λ_{scr} . Within this distance of the filament, the medium supplies an antiparallel screening supercurrent $-I$, so that at greater distances from the source filament than λ_{scr} , the magnetic field goes quickly to zero. Within the screening region of depth λ_{scr} , the magnetic field of the current will be of order $2I/c\lambda_{\text{scr}}$, which implies a vector potential \mathbf{A} (parallel to the filament) of order $2I/c$ in the London gauge. Applying the London equations in terms of the vector potential, $\mathbf{J}_s = -(c/4\pi\lambda_{\text{eff}}^2)\mathbf{A}$, the screening current density near the source is $J_{\text{scr}} \approx -I/2\pi\lambda_{\text{eff}}^2$. In a three-dimensional bulk superconductor, the screening current flows in a circular cross section of radius λ_{eff} ; the total screening current will be of order $\pi\lambda_{\text{scr}}^2 J_{\text{scr}}$. Equating this to the source current I , we find $\pi\lambda_{\text{scr}}^2 \approx 2\pi\lambda_{\text{eff}}^2$, or $\lambda_{\text{scr}} \approx \lambda_{\text{eff}}$, as expected. We now contrast this with the case of a current filament in (or immediately above) a thin superconducting film of thickness d . The screening current density J_{scr} found above is also correct in this case, but it will flow in a cross-sectional area of only $\sim 2\lambda_{\text{scr}}d$. Equating the total screening current to the source current, we find $2\lambda_{\text{scr}}d \approx 2\pi\lambda_{\text{eff}}^2$, or

$$\lambda_{\perp} = \lambda_{\text{scr}} \approx \lambda_{\text{eff}}^2/d \quad (d \ll \lambda_{\text{eff}}) \quad (3.137)$$

within small numerical factors.

The most important application of this general result is to the current vortex associated with a quantum of flux passing through a thin film at normal incidence. As Pearl showed in his original paper, the scale at which the radial dependence of the circulating sheet current density changes from $1/r$ to $1/r^2$ is set by this λ_{\perp} . For comparison, the radial dependence of the current density in a similar vortex in *bulk* material with penetration depth λ changes from $1/r$ to an exponential cutoff at $r \sim \lambda$. Thus, one can say that the radius of a vortex expands from $\sim \lambda$ in bulk material to $\sim \lambda_{\perp}$ in a film of thickness $d < \lambda$. Moreover, in a thin film, Pearl's solution shows that the long-range falloff is only power law $\sim 1/r^2$, rather than exponential $\sim e^{-r/\lambda}$ as in bulk material.

3.11.5 Measurement of λ

Before leaving the subject of the penetration depth, we briefly review some experimental techniques which have been used to measure this quantity. The earliest experiments⁵⁵ involved use of a large number of colloidal particles or thin films with a small dimension d comparable to λ . Varying the temperature, and hence $\lambda(T)$, then caused substantial fractional changes in magnetic susceptibility, which

⁵⁵For example, D. Shoenberg, *Proc. Roy. Soc. (London)* **A175**, 49 (1940); J. M. Lock, *ibid.*, **A208**, 391 (1951).

could be measured. To the extent that the particle-size distribution of the sample was known, this allowed $\lambda(T)$ to be estimated, using (2.5), but evidently there were major quantitative uncertainties.

It was pointed out by Casimir⁵⁶ that an ac susceptibility technique should be sufficiently sensitive to allow the temperature-dependent change in field penetration [$\lambda(T) - \lambda(0)$] at the surface of a single bulk sample to be measured. This experiment was first carried out successfully by Laurmann and Shoenberg⁵⁷ by using a mutual inductance bridge operating at 70 Hz, but their sensitivity did not allow very quantitative results to be obtained. A 10-fold increase in sensitivity, allowing changes of λ at the 2 Å level to be detected, was obtained by Pippard⁵⁸ by raising the frequency to $\sim 10^{10}$ Hz and by using microwave techniques to measure the temperature-dependent shift in the resonant frequency of a cavity caused by the changes in $\lambda(T)$. This technique greatly improved his sensitivity but did require significant corrections to be made for normal electron effects which become increasingly serious at the higher frequencies. By using the normal-state skin depth as a reference, he was able to obtain a measurement of the absolute value of $\lambda(T)$, not just its change with temperature, but this was of lesser accuracy.

After the BCS theory appeared, Schawlow and Devlin⁵⁹ remeasured $\lambda(T)$ in tin, working at about 10^5 Hz, where the high-frequency corrections needed by Pippard were negligible but without loss of sensitivity because digital frequency counters had become available to improve the accuracy with which shifts in the cavity frequency could be measured. While their results generally followed the two-fluid relation that $\lambda(T) \propto y = (1 - t^4)^{-1/2}$, a plot of $d\lambda/dy$ vs. y showed a rather sharp rise of this quantity below $y \approx 1.5$. Exactly this sort of behavior was predicted by BCS because of the exponential cutoff of excitations due to the gap, which controls the detailed temperature dependence of $\lambda_L(T)$ as given by (3.111). Although there was no complete quantitative agreement between theory and experiment, this probably can be attributed to the fact that the theory is for an idealized isotropic metal, whereas tin has a complex Fermi surface, with known anisotropy in the gap and in the penetration depth. These classic high-frequency measurements of $\lambda(T)$ have been reviewed by Waldram.⁶⁰

It is important to remember that the most sensitive methods measure only *changes* in $\lambda(T)$ with temperature. As a result, quoted "experimental" values of $\lambda(0)$ are usually values inferred by fitting data to a theory of $\lambda(T)$. This is usually the old two-fluid dependence since with BCS *two* parameters, $\lambda(0)$ and ξ_0 , must be fitted.

⁵⁶H. B. G. Casimir, *Physica* **7**, 887 (1940).

⁵⁷E. Laurmann and D. Shoenberg, *Nature* **160**, 747 (1947); *Proc. Roy. Soc. (London)* **A198**, 560 (1949).

⁵⁸A. B. Pippard, *Proc. Roy. Soc. (London)* **A191**, 399 (1947); **203**, 98 (1950).

⁵⁹A. L. Schawlow and G. E. Devlin, *Phys. Rev.* **113**, 120 (1959).

⁶⁰J. R. Waldram, *Adv. Phys.* **13**, 1 (1964).

The advent of the high-temperature superconductors brought a revival of interest in the measurement of $\lambda(T)$ since its absolute value gives information about n_s , and its temperature dependence is predicted to be different for different proposed underlying microscopic theories. For example, for a local clean-limit BCS superconductor with a finite gap all over the Fermi surface, $[\lambda(T)/\lambda(0) - 1]$ should go to zero exponentially as $T^{-1/2}e^{-\Delta(0)/kT}$ as $T \rightarrow 0$,⁶¹ as can be derived from (3.111). On the other hand, a superconductor with nodes in the gap has a finite density of low-lying states, and $[\lambda(T)/\lambda(0) - 1]$ should go to zero as a power law $(T/T_c)^n$, where n depends on whether the nodes are points or lines, etc.

Unfortunately, uncertainties about the surface quality of samples of these materials adds a major additional obstacle to those noted in connection with high-frequency measurements on the classic superconductors. Nonetheless, very sensitive measurements by Anlage et al.⁶² on a resonant stripline seem to indicate that $\lambda^{-2}(T)$ in YBCO follows a dependence closer to $(1 - t^2)$ than the usual two-fluid form $(1 - t^4)$. In other words, the penetration depth is varying down to lower temperatures than in the classic superconductors. In general, this implies lower-lying quasi-particle states than in BCS. This could either reflect substantial gap anisotropy, with some regions of small gap, or it could reflect unconventional pairing, which entails nodes where the gap goes to zero.

A new experimental approach, capable of absolute measurement of $\lambda(T)$ and also insensitive to surface conditions, is the use of muon spin rotation measurements to determine the distribution of local magnetic fields in a superconductor in the mixed state.⁶³ The range of field-variation scales with $1/\lambda^2(T)$, which controls the strength of the local vortex currents that produce the local field variations, allowing $\lambda(T)$ to be inferred. Although the precision of this technique is not as great as the high-frequency methods, and there are complications in the interpretation stemming from the thermal motion of the flux tubes about their ideal lattice locations, this technique has been very useful in studying the high-temperature superconductors. These results will be discussed in Sec. 9.9.3, together with other types of measurements on these interesting materials.

3.12 CONCLUDING SUMMARY

In this chapter, we have set out the basic features of the BCS theory: the Cooper pairing due to a weak, phonon-mediated attraction between electrons, the nature of the superconducting ground state and its condensation energy relative to the

⁶¹J. Halbritter, *Z. Physik* **243**, 201 (1971).

⁶²S. M. Anlage, B. W. Langley, G. Deutscher, J. Halbritter, and M. R. Beasley, *Phys. Rev.* **B44**, 9764 (1991).

⁶³See, e.g., Y. J. Uemura et al., *Phys. Rev.* **B38**, 909 (1988); D. R. Harshman et al., *Phys. Rev.* **B39**, 851 (1989); Y. J. Uemura et al., *Phys. Rev. Lett.* **62**, 2317 (1989) and **65**, 2665 (1991); C. Niedermayer et al., *Phys. Rev. Lett.* **71**, 1764 (1993); J. Sonier et al., *Phys. Rev. Lett.* **72**, 744 (1994).

normal state, the excited quasi-particle states above the energy gap, and the temperature dependence of the gap and the thermodynamic quantities. We then showed how electron tunneling has been able to confirm the density of excited states above the gap in detail, and even to confirm the quantitative correctness of the electron-phonon mechanism for setting up the superconductive state in a number of the classic superconductors. Our analysis of the transition probabilities for quasi-particle excitation and scattering gave further testimony to the correctness of the theory since very different temperature dependences were predicted and observed for ultrasonic attenuation and nuclear relaxation processes, which would have the *same* temperature dependence in a *simple* two-fluid model without the coherence factors derived from the pairing model. Finally, we have treated the electrodynamics of superconductors, first computing the absorption due to quasi-particle processes, and then computing the lossless supercurrent response in the presence of a vector potential. The latter computation confirmed the correctness of the Pippard nonlocal generalization of the London electrodynamics, and was then applied to work out predictions for the dependence of $\lambda(T)$ on λ_L , ξ_0 , and ℓ .

Having seen that the BCS theory provides a microscopic foundation for the relatively simple semimicroscopic or phenomenological London and Ginzburg-Landau theories of superconductivity, we now use the latter to explore numerous superconducting phenomena. This program will occupy most of the remaining chapters of this book.