

ing crowdion, "body-centered," or "A" interstitial positions the calculations show that the interstitial returns to its position in configuration "B". Configuration "B" is separated from possible surrounding interstitial configurations by energy barriers of about 0.3 ev.

The interstitial configuration with the interstitial in the "body-centered" position is found to be unstable. Calculations performed with V_1 and V_M show that the interstitial moves from the elementary cube center along a cubic axis about $0.2a$ into the equilibrium configuration "A". The migration energy for an interstitial moving between adjacent "A" configurations turns out to be 0.1 ev. Furthermore, the crowdion is found to be unstable. Using V_1 or V_M the extra atom of the crowdion configuration moves into a next neighbor position which is equivalent to the interstitial position in configuration "A." These results agree with those found with the potential V_1 by Gibson *et al.*⁶

The number of atoms around the interstitial treated

as movable discrete particles is about 150 for the interstitial configuration "A" and about 50 for the interstitial configuration "B". Using potential V_1 , the change in volume of the crystal arising from the interstitial is found to be 1.126 atomic volumes for configuration "A" and 1.432 atomic volumes for configuration "B". The contributions to the formation energy of an interstitial arising from the potential V_1 turn out to be 3.548 ev for configuration "A" and 4.098 ev for configuration "B".

A more detailed description of the calculations is given in a paper which will be published in the *Zeitschrift für Physik*.

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Theory of Many-Particle Systems. II. Superconductivity*

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A fermion system with a simple attractive interaction is discussed with the aid of time-dependent correlation functions. Although perturbation theory is inapplicable, a sequence of correlation approximations described in the first paper of this series can be employed. The lowest approximation in the sequence expresses the two-particle correlation function in terms of single-particle functions and leads to the Hartree approximation; the second expresses three-particle correlation function in terms of one- and two-particle correlation functions and leads to the time-dependent correlation functions that characterize the superconducting model of Bardeen, Cooper, and Schrieffer. In the second section of this paper these correlation functions are determined and the thermodynamic properties of the superconductor are calculated from them.

In the third section of the paper, the electromagnetic effects of the superconductor predicted by the Bardeen-Cooper-Schrieffer time-dependent correlation functions are considered. Their un-

satisfactory description of current conservation is indicated and overcome in the fourth section by a more accurate solution valid at nonvanishing temperature. This solution predicts different diffusive properties but the same Meissner effect and superconductive behavior, since the longitudinal current correlation function is modified while the transverse current correlation function is not.

The fifth section of the paper is devoted to the properties of a pure superconductor which depend on the lifetimes of the single-particle excitations. The effect of these lifetimes on the static electrical conductivity is determined, and it is shown that they do not destroy supercurrents although they eliminate a gap in the single-particle excitation spectrum. Their effect on the thermal conductivity is also calculated using heat current correlation functions. It is shown that a model which treats the lifetime of the single-particle excitation due to lattice interactions as constant yields results in agreement with observed thermal conductivities.

1. INTRODUCTION

IN a previous paper,¹ a formalism for discussing systems with many particles was developed, and certain systematic approximation techniques were outlined. A sequence of relative approximations which did not involve expansion in powers of the potential was pro-

posed and shown to yield many of the features which characterize these many-particle systems. Before extending this general formulation, it seems desirable to illustrate the techniques introduced by applying them to a specific problem. Probably the most illuminating example on which to employ them is a simplified model of superconductivity. On the one hand, this example provides a rather stringent test of any approximation scheme, since the model is known to have features which cannot be derived by expansion in the coupling constant. On the other hand, the application of a

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¹ P. C. Martin and J. Schwinger, Phys. Rev. 115, 1342 (1959), hereafter referred to as I.

general approximation procedure² yields additional insight into the results which have been derived for this model and indicates how they may be extended. Using this approach, we shall rederive many properties of the superconductor which have been previously computed and calculate some additional properties like the temperature-dependent electrical and thermal conductivities.

The model of a superconductor which we consider is similar to the one originally proposed by Bardeen and co-workers.³ The conclusions we derive are identical with those derived by BCS and other authors.⁴ In obtaining their results, they introduced a certain pairing condition. One of our aims is to infer that condition from the simple, but reasonable, interaction originally proposed. We show that perturbation theory can only be applied to the pair correlation approximation above a critical temperature. Below this temperature, perturbation theory leads to an unstable correlation function for particles of opposite spin; however, a nonperturbative, stable solution involving a Bose condensation of pairs can be derived within the pair correlation approximation. From this solution, which is identical with the one proposed by BCS, the various thermodynamic properties of a superconductor are readily obtained. A more accurate solution which takes some intrinsic three-particle correlations into account is also derived. This solution, similar at vanishing temperature to the one discussed by Anderson⁵ and Rickayzen,⁶ satisfies the current conservation condition and consequently predicts gauge-invariant dielectric properties. In this more accurate solution, certain long-wavelength matrix elements of the density are substantially altered. The more correct matrix elements oscillate with the sound-wave frequency at vanishing temperature in a neutral superconductor. As the temperature rises, these modes become unstable, disintegrating into single-particle excitations. The Coulomb interaction has an overwhelming effect on the oscillation frequencies.⁷ It leads in the usual fashion to a dominance of the plasma frequency in the longitudinal mode with a corresponding

reduction of the low-frequency oscillations characteristic of the neutral system.⁸

The most interesting features of a superconductor are its electromagnetic properties. In I, a general method was discussed for determining these properties of a many-particle system from the correlation functions that describe the system when no electromagnetic field is present. Using this method, we determine the current induced in a superconductor by arbitrary externally applied scalar and vector potentials. Questions involving gauge invariance are eliminated with the more accurate approximation, since it leads to a current correlation function which conserves charge and a frequency-dependent conductivity which satisfies the longitudinal sum rule.⁹ In this more accurate solution, only the longitudinal modes are modified. Consequently, predictions of superconductivity and the Meissner effect, described by the transverse conductivity, are unaffected.

One feature of our discussion is the appearance of lifetimes for single-particle excitations and collective modes. In an interacting system measurements generally lead to excitations of so many states that the number in an infinitesimal energy range is infinitesimal. As a consequence, the average subsequent responses are characterized by finite lifetimes. While these lifetimes cannot be included in an effective single particle model Hamiltonian they may be naturally introduced into the equations from which we calculate the time-dependent correlation functions describing the system.

Determination of the transport properties depends on the inclusion of these single-particle excitation lifetimes. Using them, we determine various transport properties in terms of correlation functions of conserved currents. In particular, we discuss the correlation functions which describe thermal conductivity and diffusion in a superconducting system.

2. CORRELATION FUNCTIONS OF A SUPERCONDUCTOR

Although a real superconductor contains an ion (or phonon) field coupled to the electrons, the model we

² A preliminary discussion of this approach was presented by A. Cantor and P. C. Martin, *Bull. Am. Phys. Soc.* **3**, 202 (1958).

³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957), hereafter referred to as BCS.

⁴ N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *New Methods in the Theory of Superconductivity* (Academy of Sciences of the U.S.S.R., Moscow, 1958); J. G. Valatin, *Nuovo cimento* **7**, 843 (1958); L. P. Gor'kov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 735 (1958); [translation: *Soviet Phys.-JETP* **34**, 505 (1958)]; A. A. Abrikosov, L. P. Gor'kov, and I. M. Khalatnikov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 265 (1958) [translation: *Soviet Phys.-JETP* **35**, 182 (1959)]; A. A. Abrikosov and L. P. Gor'kov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 1558 (1958) [translation: *Soviet Phys.-JETP* **35**, 1090 (1959)]; and several other authors.

⁵ P. W. Anderson, *Phys. Rev.* **112**, 1900 (1959).

⁶ G. Rickayzen, *Phys. Rev.* **115**, 795 (1959).

⁷ The importance of the Coulomb interaction in suppressing low-lying longitudinal modes has been stressed by Anderson. In our discussion it will appear that there is complete elimination only in the zero-wavelength mode at vanishing temperature. However as we might anticipate, most of the oscillator strength for small wavelength lies at the plasma frequencies at all temperatures.

⁸ In the weakly interacting Fermi gas these oscillations are known as zero sound. In the neutral superconductor they would correspond to ordinary sound.

⁹ The problems of gauge invariance have been discussed at great length. See, for example, P. W. Anderson, *Phys. Rev.* **110**, 827 (1958); M. J. Buckingham, *Nuovo cimento* **5**, 1763 (1957); M. R. Schafroth, *Helv. Phys. Acta* **24**, 645 (1951). We shall show that an approximate calculation of electromagnetic properties will be gauge invariant if it leads to diagonal two-particle matrix elements which satisfy the current conservation condition and the longitudinal sum rule. This sum rule can be expressed in terms of two matrix elements of the density, two matrix elements of the current, or one of the current and one of the density. Even inaccurate calculations generally satisfy the sum rule in the last form, since that form only depends on the equal-time commutation relations. The BCS matrix elements, in particular, satisfy the sum rule in this form [Eq. (3.8)]. The more usual statements of the sum rule in terms of two current matrix elements or two charge-density matrix elements also invoke current conservation and therefore it should be no surprise that they test gauge invariance.

consider predicates that the important effect of the phonons can be effectively simulated by a nonlocal electron-electron coupling $\langle |v| \rangle$, and consequently that the system can be characterized by a Hamiltonian H of the form

$$\begin{aligned} H &= H_0 + H_I; \\ H_0 &= \sum \int \psi^\dagger(\mathbf{r}s) (-\nabla^2/2m) \psi(\mathbf{r}s), \\ H_I &= \frac{1}{2} \sum \int \langle \mathbf{r}_1 s_1 \mathbf{r}_2 s_2 | v | \mathbf{r}_3 s_3 \mathbf{r}_4 s_4 \rangle \\ &\quad \times \psi^\dagger(\mathbf{r}_1 s_1) \psi^\dagger(\mathbf{r}_2 s_2) \psi(\mathbf{r}_3 s_3) \psi(\mathbf{r}_4 s_4). \end{aligned} \quad (2.1)$$

The summation and integration extend over all coordinate indices of the spin- $\frac{1}{2}$ electron field ψ : the spatial coordinates \mathbf{r} and the coordinates which denote the component of spin along the axis of quantization s . The latter takes on two values which we label $+$ and $-$.

We discuss the properties of this system of particles in terms of time-dependent field correlation functions. In particular, we employ the Green's functions which are expectation values of time-ordered products of creation and annihilation operators in a grand canonical ensemble. This ensemble is characterized by two parameters—the inverse temperature β in energy units, and the chemical potential μ —or equivalently, by β and $\alpha = -\beta\mu$. The definition of the Green's functions and other quantities, and the notations and conventions conform with those employed in I. We deviate slightly by writing the spin coordinate of the Fermi field explicitly. Since the Hamiltonian conserves total spin, the only nonvanishing Green's functions are those in which the number of creation operators whose spin lies parallel to the axis of quantization is equal to the number of annihilation operators with spin in that direction.

Many of the important features of this model can be characterized in terms of the one- and two-particle correlation functions. The latter has two forms, the first, $G_2(1+, 2-; 1'+, 2'-)$, describing the correlation between particles of opposite spin, and the second, $G_2(1+, 2+; 1'+, 2'+)$, describing the correlation between particles of the same spin. We may denote these more concisely as $G^{+-}(12; 1'2')$ and $G^{++}(12; 1'2')$, and correspondingly omit spin indices from the one-particle function $G_1(1+; 1'+)$. Indeed, taking translational invariance into account, we may write $G_1(1; 1')$ in the form $G(1-1')$.

In order to determine G_1 and G_2 , we introduce an extremely simplified interaction which enables us to carry through the procedures of calculation outlined in I. The potential V in this interaction,

$$H_I = -\frac{1}{2} \sum \int V \psi^\dagger(\mathbf{r}s_1) \psi^\dagger(\mathbf{r}s_2) \psi(\mathbf{r}s_2) \psi(\mathbf{r}s_1), \quad (2.2)$$

is implicitly understood to project out only those parts of the field operators whose momentum \mathbf{p} lies in a small range, $(|p^2 - p_F^2|/2m) < \omega_D$, of the Fermi momentum p_F .¹⁰ The symbol ω_D is intended to suggest that the range of attractive interaction in a conductor is effectively governed by the Debye frequency. Conductors are supposed to differ from one another as a result of the dominance or unimportance of this attractive interaction in comparison with Coulomb or other couplings.¹¹

The introduction of such a momentum-space cutoff in the interaction potential has the effect of removing divergences and spreading out the simple point potential. For most purposes this cutoff is inessential, and it shall consequently be ignored when unnecessary. The implicit notation in (2.2) forebodes this suppression.

The characterization of the Green's functions by an infinite set of coupled equations with boundary conditions was discussed in I. The first two equations in this hierarchy were written in the form¹²

$$\begin{aligned} [i(\partial/\partial t_1) + (\nabla_1^2/2m)]G(1-1') \\ = \delta(1,1') + iVG^{+-}(11; 1'1^+), \end{aligned} \quad (2.3)$$

and

$$\begin{aligned} [i(\partial/\partial t_1) + (\nabla_1^2/2m)]G^{s_1 s_2}(12; 1'2') \\ = G(2-2')\delta(1,1') - G(2-1')\delta(1s_1, 2's_2) \\ + iVG_2(1s_1, 2s_2, 1-s_1; 1's_1, 2's_2, 1^+-s_1). \end{aligned} \quad (2.4)$$

A single self-consistent Hartree-Fock equation was obtained as a first approximation when the two-particle correlation function was replaced by one which neglected intrinsic two-particle effects. A closed pair of equations was correspondingly obtained in a second approximation. That approximation involved neglecting intrinsic three-particle correlations by expressing the three-particle correlation function in terms of the one- and two-particle correlation functions. One method of replacement of G_3 was discussed in I, where an appropriate combination of one- and two-particle Green's functions was shown (cf. 6.13) to consist of the antisymmetrized product of one-particle correlation functions together with terms containing all permutations of arguments of one-particle correlation functions multiplied by differences between one- and two-particle correlation functions. For the interaction we have

¹⁰ This interaction in which the potential is a constant times a projection operator which selects momenta near the surface of the Fermi sea was originally proposed by Gor'kov, reference 4. The Gor'kov interaction is a simplified version of the Hamiltonian with which BCS began. However, it is much more similar to the true electronic interaction than the truncated Hamiltonian that was employed in the BCS computations.

¹¹ We inquire no further into the criteria for superconductivity.

¹² In these expressions, the *superscript* $+$ determines the ordering of the operators which refer to the same point. This superscript should not be confused with the spin indices which have been suppressed except in G_3 which shall be eliminated momentarily.

assumed, this approximation reduces to

$$\begin{aligned}
 G_3(1s_1, 2s_2, 1-s_1; 1's_1, 2's_2, 1^+-s_1) \\
 \cong G(2-2')G^{+-}(11; 1'1^+) \\
 -\delta(s_1, s_2)G(2-1')G^{+-}(11; 2'1^+) \\
 -\delta(s_1, -s_2)G(2-1)G^{+-}(11; 1'2') \\
 +G(1-1^+)L^{s_1s_2}(12; 1'2') \\
 +\delta(s_1s_2)G(1-1^+)G(1-2')G(2-1') \\
 -\delta(s_1s_2)G(1-2')L^{+-}(21; 1'1) \\
 -\delta(s_1, -s_2)G(1-2')L^{+-}(12; 1'1) \\
 +G(1-1')L^{-s_1s_2}(12; 1^+2') \\
 +\delta(s_1, -s_2)G(1-1')G(2-1^+)G(1-2'). \quad (2.5)
 \end{aligned}$$

In (2.5) we have introduced the symbol $L^{s_1s_2}$,

$$\begin{aligned}
 L^{s_1s_2}(12; 1'2') = G^{s_1s_2}(12; 1'2') \\
 -G(1-1')G(2-2'), \quad (2.6)
 \end{aligned}$$

for the correlated part of G_2 and have taken into account the fact that $\psi(1s)^2=0$ because of the exclusion principle.

We may simplify the analysis of the problem by anticipating the irrelevance in a first approximation of all save the first four terms in (2.5). Inserting these terms in Eq. (2.6) into Eqs. (2.3) and (2.4), we obtain the equations

$$\tilde{G}^{-1}[G(1-1')-\tilde{G}(1-1')]=iVL^{+-}(11; 1'1^+), \quad (2.7)$$

$$\tilde{G}^{-1}L^{+-}(12; 1'2')=-iVG(2-1)G^{+-}(11; 1'2'), \quad (2.8)$$

and

$$L^{++}(12; 1'2')=-G(1-2')G(2-1'), \quad (2.9)$$

where the operator, \tilde{G}^{-1} , is the inverse single-particle Green's function in the Hartree approximation,

$$\tilde{G}^{-1}=(i\partial/\partial t)+(\nabla^2/2m)-iVG(1-1^+). \quad (2.10)$$

The combination $-iVG(1-1^+)$ is equal to the potential strength times the number of particles interacting with a given one. This term represents an average constant potential due to the particles and is equal, in the zero temperature limit, to $V\omega_D m p_F/2\pi^2 \equiv \frac{1}{2}V\omega_D \rho_E$. Although this shift is considerably larger than the displacements we shall consider momentarily, it represents a trivial effect which is completely accounted for by changing the chemical potential from its free-particle value, $\mu=p_F^2/2m$. Indeed, it is convenient to shift the origin of energy to

$$\mu=(p_F^2/2m)-iVG(1-1^+) \quad (2.11)$$

to introduce the variable

$$\epsilon(p)=(p^2-p_F^2)/2m, \quad (2.12)$$

and to measure frequencies relative to the chemical potential so that the Fourier transform of \tilde{G}^{-1} becomes

$$\tilde{G}^{-1}(\epsilon, \omega)=\omega-\epsilon. \quad (2.13)$$

The definition of the singularity in the Fourier

transformation of G was discussed in I. It was shown there that its Fourier transform with respect to space-time difference variables could be represented in the form

$$G(\epsilon, \omega)=\int \frac{d\omega'}{2\pi} \left[P \frac{1}{\omega-\omega'} - \pi i \delta(\omega-\omega') \tanh \frac{1}{2} \beta \omega \right] A(\epsilon, \omega), \quad (2.14)$$

with

$$A(\epsilon, \omega) \geq 0 \quad \text{and} \quad \int \frac{d\omega}{2\pi} A(\epsilon, \omega) = 1. \quad (2.15)$$

This representation followed from the periodicity of the function G_1 in the imaginary time variable. An analogous periodicity was shown to hold for the function G_n in I, and the significance of this periodicity was discussed. Briefly, it was pointed out that the differential equations (2.4) and the approximations (2.5) make no reference to the particular thermodynamic average we want the Green's functions to represent. They are equally true differential equations for arbitrary matrix elements of the field operators. It is only by the boundary conditions on these differential equations that the thermodynamic average matrix elements are specified. Because the average matrix element is a trace, and the Boltzmann factor $e^{-\beta H}$ is equivalent to an imaginary time translation, it is possible to characterize the thermodynamic Green's function solutions to the differential equations by its equality under imaginary translation of a single time argument. This boundary condition is most easily imposed on the general time-ordered function G_n by rotating all times to the imaginary axis or letting $\beta \rightarrow i\tau$. Then identity under translation and time ordering can be described in terms of properties of a function of real variables restricted to the interval $[0, \tau]$. This translational property is naturally expressed with the aid of Fourier series. After the Green's functions are obtained they must be extended to real times and real temperatures by rotating back and analytically continuing to time differences outside the interval $[0, \tau]$.

To obtain solutions to (2.7) and (2.8) which satisfy this periodicity requirement, we employ the Green's function \tilde{G} which exhibits this periodicity and integrate over one period. Thus we write

$$\begin{aligned}
 G(1-1') = \tilde{G}(1-1') \\
 + i \int d\bar{1} \tilde{G}(1-\bar{1}) V L^{+-}(\bar{1}\bar{1}; 1'\bar{1}^+), \quad (2.7')
 \end{aligned}$$

where the time integration extends from $\bar{t}_1=0$ to $\bar{t}_1=-i\beta$, and similarly,

$$\begin{aligned}
 L^{+-}(12; 1'2') \\
 = -i \int d\bar{1} \tilde{G}(1-\bar{1}) G(2-\bar{1}) V G^{+-}(\bar{1}\bar{1}; 1'2'). \quad (2.8')
 \end{aligned}$$

Since \tilde{G} is a function with the properties of G , its Fourier transform may be expressed in the form (2.14) with

$$\begin{aligned}\tilde{A}(\epsilon, \omega) &= 2\pi\delta(\omega - \epsilon), \\ \tilde{G}(\epsilon, \omega) &= P[1/(\omega - \epsilon)] - \pi i\delta(\omega - \epsilon) \tanh(\beta\epsilon/2).\end{aligned}\quad (2.16)$$

For the purpose of solving the integral equations (2.7') and (2.8'), we replace the integral representation by a Fourier series representation. We first investigate whether there is an approximate solution to these equations which is similar to the noncorrelative solution $L^+ \cong 0$, $\tilde{G} \cong G$ appropriate to the noninteracting system. The consistency of such a solution is easily tested since L^{+-} can be immediately determined by (2.8') with G replaced by \tilde{G} . As in I, we introduce $L^{+-}(\mathbf{p}, \omega_\nu)$ where $\omega_\nu = i\pi\nu/\beta$, and ν is an even integer,

$$L^+(11; 1'1') = -\frac{1}{i\beta} \sum_{\nu} \exp[-i\omega_\nu(t_1 - t_1')] \int \frac{d\mathbf{p}}{(2\pi)^3} \times \exp[i\mathbf{p} \cdot (\mathbf{r}_1 - \mathbf{r}_1')] L^{+-}(\mathbf{p}, \omega_\nu)$$

and

$$\begin{aligned}L^{+-}(\mathbf{p}, \omega_\nu) &= \int_0^{-i\beta} d(t_1 - t_1') \int d(\mathbf{r}_1 - \mathbf{r}_1') \\ &\times \exp[i\omega_\nu(t_1 - t_1')] \exp[-i\mathbf{p} \cdot (\mathbf{r}_1 - \mathbf{r}_1')] \\ &\times L^{+-}(11; 1'1').\end{aligned}\quad (2.17)$$

The solution to (2.8') then becomes

$$\begin{aligned}L^{+-}(\mathbf{p}, \omega_\nu) &= \Omega(\mathbf{p}, \omega_\nu) \int dt \int d\mathbf{r} \exp[-i\mathbf{p} \cdot \mathbf{r} + i\omega_\nu t] \\ &\times \int d\mathbf{r}' \int dt' (-iV) [\tilde{G}(\mathbf{r} - \mathbf{r}', t - t') \tilde{G}(\mathbf{r}' t')^2],\end{aligned}\quad (2.18)$$

with the factor $\Omega(\mathbf{p}, \omega_\nu)$ defined by

$$\begin{aligned}[\Omega(\mathbf{p}, \omega_\nu)]^{-1} &= 1 + X(\mathbf{p}, \omega_\nu), \\ X(\mathbf{p}, \omega_\nu) &= iV \int d\mathbf{r} \int dt \exp[-i\mathbf{p} \cdot \mathbf{r} + i\omega_\nu t] \\ &\times [\tilde{G}(\mathbf{r} t)]^2.\end{aligned}\quad (2.19)$$

On introducing the Fourier series representation for G and performing the trivial integrations, we obtain

$$\begin{aligned}X(\mathbf{p}, \omega_\nu) &= iV \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{i}{\beta} \sum_{\nu'} [\epsilon(\frac{1}{2}\mathbf{p} + \mathbf{q}) - \frac{1}{2}(\omega_\nu + \omega_{\nu'})]^{-1} \\ &\times [\epsilon(\frac{1}{2}\mathbf{p} - \mathbf{q}) - \frac{1}{2}(\omega_\nu - \omega_{\nu'})]^{-1},\end{aligned}\quad (2.20)$$

where ν' is an odd integer. The result of the ν' summation is

$$\begin{aligned}X(\mathbf{p}, \omega_\nu) &= V \int \frac{d\mathbf{q}}{(2\pi)^3} [\epsilon(\frac{1}{2}\mathbf{p} + \mathbf{q}) + \epsilon(\frac{1}{2}\mathbf{p} - \mathbf{q}) - \omega_\nu]^{-1} \\ &\times \frac{1}{2} [\tanh \frac{1}{2}\beta\epsilon(\frac{1}{2}\mathbf{p} + \mathbf{q}) + \tanh \frac{1}{2}\beta\epsilon(\frac{1}{2}\mathbf{p} - \mathbf{q})].\end{aligned}\quad (2.21)$$

For momentum transfers much smaller than p_F , we may take $q \approx p_F$ and introduce the approximation

$$\begin{aligned}\epsilon_{\pm} &\equiv \epsilon(\frac{1}{2}\mathbf{p} \pm \mathbf{q}) \cong \epsilon(\mathbf{q}) \pm \frac{1}{2}p_F z [\partial\epsilon(\mathbf{q})/\partial q] \\ &= \epsilon(\mathbf{q}) \pm \frac{1}{2}p_F v_F z.\end{aligned}\quad (2.22)$$

The function $X(\mathbf{p}, \omega_\nu)$ is largest for small values of p and reduces to

$$X(0, \omega_\nu) = V \rho_E \int_{-\omega_D}^{\omega_D} \frac{d\epsilon(\mathbf{q})}{2\epsilon(\mathbf{q}) - \omega_\nu} \tanh \frac{1}{2}\beta\epsilon(\mathbf{q}).\quad (2.23)$$

The function $L^{+-}(\mathbf{p}=0, t)$ is therefore equal to

$$L^{+-}(\mathbf{p}=0, t) = -\frac{1}{i\beta} \sum_{\nu} e^{-i\omega_\nu t} \frac{i}{V} X^2(0, \omega_\nu) \Omega(0, \omega_\nu).\quad (2.24)$$

To invert the Fourier series, we use the technique introduced in I. We let $\omega_\nu = \omega$ in the summand and multiply by $(1 - e^{\beta\omega})^{-1}$ for $t > 0$ and $(1 - e^{-\beta\omega})^{-1}$ for $t < 0$. Integration over a contour surrounding the singularities of $(1 - e^{\pm\beta\omega})^{-1}$ yields the summation. Since the integrand vanishes at infinity, the integral may be deformed to pass around the singularities of $X^2\Omega$ in the ω plane. As a consequence $L^{+-}(0, t)$, the probability amplitude for creating a pair of particles with total momentum zero and time zero and destroying them at time t , is represented by the line integral

$$\begin{aligned}L^{+-}(0, t) &= \int \frac{d\omega}{c2\pi} \frac{1}{V} \{X^2(1 + X)^{-1}[0, \omega_\nu \rightarrow \omega]\} \frac{e^{-i\omega(t-t')}}{e^{\beta\omega} - 1}\end{aligned}\quad (2.25)$$

over a contour which includes the singularities of the bracketed part of the integrand. When the poles of the bracketed expression are on the real axis and the integrand is bounded at infinity, $L^{+-}(0, t)$ behaves in an admissible manner, oscillating or decreasing as $t \rightarrow \infty$. This is true, for example, of the spatial Fourier transform $X(\mathbf{p}, t)$, of $[\tilde{G}(\mathbf{r}, t)]^2$, and of X^2 , the Born approximation to $L(\mathbf{p}, t)$. We might therefore expect (2.25) to be approximately correct in the weak coupling limit. In particular, since there exists a dimensionless parameter containing the potential, $V\rho_E$, it might be expected that (2.25) would be accurate with $\Omega \cong 1$ for $V\rho_E \ll 1$. This is not the case: At low enough temperatures an arbitrary weak attractive interaction results in an unstable solution for $L(0, t)$.

A necessary condition for the stability of $L(\mathbf{p}, t)$ is that the bracketed expression in (2.25) have no poles for values of ω off the real axis. This condition must be satisfied, since poles of the correlation function correspond to energy differences between states of the system and must consequently be real. However, a pole of $L(\mathbf{p}, \omega)$ will appear whenever the function of a complex variable ω , $X(\mathbf{p}, \omega)$, is equal to minus one. If the interaction is repulsive, $X(\mathbf{p}, \omega)$ will never equal minus one.

If, however, the interaction is attractive and weak, there will be two imaginary values of ω for which $1+X(0,\omega)=0$ at zero temperature. They correspond to complex energy differences or real exponential time dependences, and indicate that the solution (2.25) is unstable. (See Fig. 1.)

In order to see this instability in more detail, we consider the function $X(0,\omega)$ defined by (2.23):

$$X(0,\omega) = -V\rho_E \int_0^{\omega_D} d\epsilon \frac{\epsilon}{\epsilon^2 - \frac{1}{4}\omega^2} \tanh \frac{1}{2}\beta\epsilon. \quad (2.26)$$

If the interaction is repulsive, V is negative and the equation $1+X(0,\omega)=0$ cannot be satisfied for $|\omega| \ll |\omega_D|$. If the interaction is attractive, V is positive and the equation $1+X(0,\omega)=0$ cannot be satisfied at high temperatures but a pair of pure imaginary roots exist at low temperatures. These solutions move inward along the imaginary frequency axis as the temperature increases or as ρ^2 increases. They exist for sufficiently small values of ρ^2 whenever the temperature β^{-1} is smaller than the critical value β_c^{-1} at which

$$1+X(0,0)=0, \quad (2.27)$$

or more explicitly,

$$1 = V\rho_E \int_0^{\omega_D} \frac{d\epsilon}{\epsilon} \tanh \frac{1}{2}\beta_c \epsilon. \quad (2.28)$$

Since the assumption of small correlation leads to instabilities for $\beta > \beta_c$ and $V < 0$, we conclude that if the potential is attractive, this assumption is only tenable above the critical temperature. We therefore consider afresh Eqs. (2.7) and (2.8) for attractive potentials at low temperatures.

At the onset of instability, there is an eigenfunction with $\omega=0$, of the equation for L . This implies that some matrix elements of the form

$$\langle NE\xi | \psi_s \psi_{-s} | N-2, E-2\mu, \xi' \rangle$$

persist for infinitely long times. This suggests that at lower temperatures similar matrix elements in a decomposition of $L^{+-}(12;1'2')$ with the unprimed annihilation field points greatly separated from the primed field creation points might be as important as the terms $G(12')G(21')$. We therefore inquire into the possibility of a stable solution with these primed and unprimed points greatly separated. In investigating this asymptotic limit, we ignore the inhomogeneous term

$$-i \int d\bar{1} d\bar{2} \tilde{G}(1-\bar{1})G(2-\bar{1})V\tilde{G}(\bar{1}-1')G(\bar{1}-2'), \quad (2.29)$$

and write (2.8) in the form

$$L^{+-}(12;1'2') = -i \int d\bar{1} d\bar{2} \tilde{G}(1-\bar{1})G(2-\bar{1})VL^{+-}(\bar{1}\bar{1};1'2'). \quad (2.30)$$

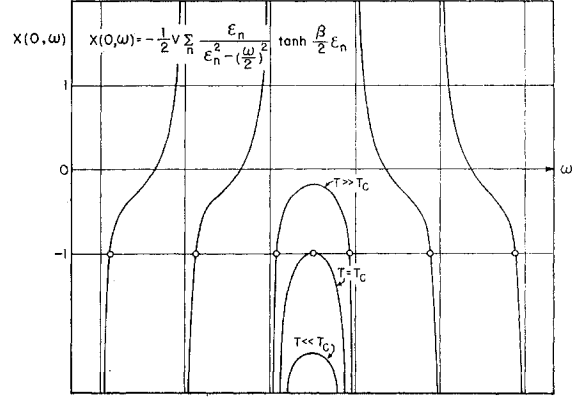


FIG. 1. To see how complex poles appear in $\Omega(0,\omega)$, we suppose that the system is confined to a finite region so that k has discrete values. In that case the integral for $X(0,\omega)$ in Eq. (2.26) is replaced by a summation over discrete values ϵ_n . At high temperatures, poles appear in $\Omega = [1+X(0,\omega)]^{-1}$ at real values of ω quite close to the values of ϵ_n . As the temperature decreases, the position of all save two of these poles is substantially unchanged. These two lowest frequency poles approach one another as the temperature decreases and coalesce at T_c . Below T_c the poles disappear for real values of ω but they appear as complex poles. These complex poles are the mathematical manifestation of the instability which leads to the superconducting state.

In virtue of the Hermitian character of the Green's functions, (2.30) may be iterated:

$$L^{+-}(12;1'2') = -V^2 \int d\bar{1} \int d\bar{1}' \tilde{G}(1-\bar{1})G(2-\bar{1}) \times L^{+-}(\bar{1}\bar{1};\bar{1}'\bar{1}')\tilde{G}(\bar{1}'-1')G(\bar{1}'-2'). \quad (2.31)$$

One solution to (2.30), (2.7), and (2.9) is obtained in the following manner: Let us suppose that $L^{+-}(11;22)$ is independent of the separation between 1 and 2. We denote the value of this constant at the temperature T by

$$L^{+-}(11;22) = -\Delta_T^2/V^2. \quad (2.32)$$

The constant Δ_T^2 must be real, since L represents the difference between the Hermitian negative definite matrices, $G^{+-}(11;22)$ and $G(1-2)G(2-1)$, and is diagonal. A more physical picture of the meaning of L^{+-} and the reality requirements on Δ_T^2 is obtained when the points 1 and 2 are set equal. With this identification the expression (2.32) becomes

$$\langle (n^+ - \langle n^+ \rangle)(n^- - \langle n^- \rangle) \rangle = \Delta_T^2/V^2, \quad (2.33)$$

where $n^\pm(\mathbf{r}t) = \psi^\dagger(\mathbf{r}t \pm) \psi(\mathbf{r}t \pm)$ is the density operator for particles with \pm spin orientation. This physical interpretation also insures that Δ_T^2 is real. It further suggests that Δ_T^2 is positive since an attractive interaction between particles of opposite spin should induce a positive correlation. Pursuing the assumption (2.32), we find that

$$L^{+-}(12;1'2') = F(1-2)F(1'-2'), \quad (2.34)$$

where we have suppressed the T dependence of Δ_T and introduced

$$F(1-2) = \Delta \int dT \tilde{G}(\bar{1}-1) G(\bar{1}-2). \quad (2.35)$$

This equation is consistent with (2.30) and (2.32) if

$$-iVF(0) = \Delta. \quad (2.36)$$

It will emerge that this condition can be satisfied below a critical temperature at which Δ vanishes. The critical temperature thus defined is identical with the one determined in (2.28) by the appearance of complex poles. Below this temperature, Eq. (2.36) serves to determine the particular nonvanishing value of Δ for which (2.30) and (2.7) have a consistent solution.

We derive the solution by introducing (2.32) into (2.7), thus obtaining

$$\begin{aligned} \tilde{G}^{-1}[G(1-1') - \tilde{G}(1-1')] \\ = -\Delta^2 \int d\bar{1} G(1-\bar{1}) \tilde{G}(1'-\bar{1}). \end{aligned} \quad (2.37)$$

The Fourier transform of this equation is

$$[\omega_\nu - \epsilon] G(\epsilon, \omega_\nu) - 1 = \Delta^2 [\omega_\nu + \epsilon]^{-1} G(\epsilon, \omega_\nu). \quad (2.38)$$

The nature of the singularities in the inversion of (2.38) may be ascertained from the integral representation (2.14). Alternatively, the boundary conditions determining the inversion may be included by utilizing the Fourier series analog of (2.38) and using a contour integral representation to express the resultant Fourier summation [cf. I, Eqs. (5.22)–(5.32)]. By either procedure we obtain the spectral function

$$A(\epsilon, \omega) = 2\pi |\omega + \epsilon| \delta(\omega^2 - E^2), \quad (2.39)$$

where

$$E = +(\epsilon^2 + \Delta^2)^{1/2}. \quad (2.40)$$

We may consequently write

$$\Delta G(\epsilon, \omega) = -(\omega + \epsilon) F(\epsilon, \omega), \quad (2.41)$$

where

$$F(\epsilon, \omega) = -P \frac{\Delta}{\omega^2 - E^2} + \pi i \delta(\omega^2 - E^2) \tanh \frac{1}{2} \beta E. \quad (2.42)$$

Whatever the value of Δ , the conditions of (2.15) are satisfied. Moreover, as in a Hartree approximation, the spectral function A has no width. In contrast with the Hartree example, however (and reminiscent of relativistic electron theory), there are two values of ω associated with each ϵ , namely, the two square roots, $\pm E$. When the form (2.42) is inserted in (2.36), the condition determining Δ becomes

$$1 = V \rho_E \int_0^{\omega_D} \frac{d\epsilon}{E} \tanh \frac{1}{2} \beta E, \quad (2.43)$$

which is identical with (2.28) at the critical temperature. The set of Eqs. (2.33) and (2.39)–(2.42), constitute a correlation function description of the superconducting model considered by BCS and Bogolyubov.¹³

These correlation functions provide a convenient basis for deriving the thermodynamic properties. For example, the distribution of momentum, $n(\mathbf{p})$, is immediately written as [cf. I, Eq. (3.68)]

$$\begin{aligned} n(\mathbf{p}) &= \int \frac{d\omega}{2\pi} \frac{\text{tr} A(\mathbf{p}, \omega)}{e^{\beta\omega} + 1} \\ &\cong 1 - \frac{\epsilon}{E} + \frac{2\epsilon}{E} \frac{e^{-\beta E}}{1 + e^{-\beta E}}, \end{aligned} \quad (2.44)$$

and the energy per unit volume, (V) , is given by [cf. I, Eq. (3.69)]

$$\begin{aligned} \frac{E}{(V)} &= \int \frac{d\mathbf{p}}{(2\pi)^3} \int \frac{d\omega}{2\pi} \frac{1}{2} \left(\omega + \epsilon + \mu + \frac{p^2}{2m} \right) \frac{\text{tr} A(\mathbf{p}, \omega)}{e^{\beta\omega} + 1} \\ &\cong \frac{3}{5} \frac{p_F^2}{2m} \frac{N}{(V)} - \frac{1}{4} V (\omega_D \rho_E)^2 + \omega_D^2 \rho_E \\ &\quad - \rho_E \int_0^{\omega_D} d\epsilon \frac{\epsilon^2 + E^2}{E} \tanh \frac{1}{2} \beta E. \end{aligned} \quad (2.45)$$

In order to compare these equations with BCS at arbitrary temperatures we first note the identity of (2.43), which determines Δ , and BCS [reference 3, Eq. (3.27)]. We have used the symbols Δ and ρ_E in place of ϵ_0 and $N(0)$, but the equations are otherwise identical. We complete the comparison by observing that the specific heat derived from (2.45) is also identical with that obtained by BCS and Bogolyubov.¹⁴ The derivative of (2.45) with respect to β may be rewritten in the form

$$\frac{d}{d\beta} \left[\frac{E}{(V)} \right] = -4\rho_E \int_0^{\omega_D} d\epsilon \frac{e^{-\beta E}}{(1 + e^{-\beta E})^2} \left(E^2 + \frac{1}{2} \beta \frac{d\Delta^2}{d\beta} \right) \quad (2.46)$$

by using the identity obtained from the temperature derivative of the equation which determines Δ .

The connection between the solution obtained above

¹³ It may be noted that Eq. (2.8') is similar to the Bethe-Salpeter equation [J. Schwinger, Proc. Nat. Acad. Sci. U. S. 37, 425–455 (1951); E. E. Salpeter and H. A. Bethe, Phys. Rev. 84, 1232 (1951)]. The similarity has led several people to surmise that the symmetrical equation $G_2 = GG + iGG_0G_2$ solved in the same approximation would be more accurate. This surmise is not correct. The Green's functions resulting from that equation can be rejected in favor of those used in BCS by means of a variation principle [J. Goldstone (private communication)]. They can also be rejected experimentally since they give rise to a T^2 specific heat. Finally, the formal cancellation between the terms in the perturbation series resulting from the symmetrical equation and other effects omitted from the Bethe-Salpeter equation can be indicated [A. Cantor (private communication)].

¹⁴ N. N. Bogolyubov, Zubarev, and Tserkovnikov, Doklady Akad. Nauk. S.S.S.R. 117, 778 (1957).

and a Bose condensation may be simply understood.¹⁵ For a free Bose system, the spectral representation,

$$G(\mathbf{p}, \omega) = \int \frac{d\omega'}{2\pi} \left[P \frac{1}{\omega - \omega'} - \pi i \delta(\omega - \omega') \coth \frac{1}{2}(\alpha + \beta\omega) \right] \times A(\mathbf{p}, \omega'), \quad (2.47)$$

discussed in I requires an extremely singular weight function at low temperatures. Specifically, the spectral function takes the form

$$\frac{A(\mathbf{p}\omega)}{e^{\alpha+\beta\omega}-1} = \frac{2\pi\delta(\omega - p^2/2m)}{e^{\alpha+\beta\omega}-1} + (2\pi)^4 \delta(\omega) \delta(\mathbf{p}) n_0 \quad (2.48)$$

below the condensation temperature. In this expression, n_0 is a constant representing the density of particles in the lowest mode as a function of temperature. The occurrence of the parameter n_0 may be related to the coalescence of the singularities in $A(0, \omega)$ and $(e^{\alpha+\beta\omega}-1)^{-1}$. At large separations this singular contribution dominates the Green's function, giving rise to a constant value, n_0 , for $G(1-1')$. The correlation function for a pair of fermions has a spectral representation analogous to (2.47). Indeed, the function $(2\pi)^{-4} \Delta^2/V^2$ plays the same role in this representation as n_0 does in (2.48). The less singular portions of the corresponding spectral function for L have been eliminated by omitting the inhomogeneous term (2.29) of Eq. (2.8).

3. GAUGE INVARIANCE AND ELECTROMAGNETIC PROPERTIES

In the previous section, we developed approximations for the one- and two-particle Green's functions of the superconductor and we saw that these approximations led to the results originally obtained by BCS. However, the BCS theory in its original form is not gauge invariant. We should therefore not be surprised to find that the correlation functions derived in the previous section do not predict electromagnetic properties of the superconductor gauge invariantly. Before exhibiting this flaw, it is convenient to extend to a general gauge the discussion of electromagnetic transport developed in I. We shall then develop criteria which indicate when a given approximation for the correlation functions of a system leads to a gauge-invariant description of its electromagnetic properties. Finally, we use these criteria to rule out the BCS correlation functions and generate more satisfactory ones.

A. General Discussion of Electromagnetic Transport

We begin by considering a general system of charged particles described by a Hamiltonian which includes all

electromagnetic interactions between the particles. The effect of subjecting this system to externally applied electric and magnetic fields can be represented by adding to the Hamiltonian density an interaction Hamiltonian density which depends upon an external vector potential \mathbf{A}^{ext} and an external scalar potential ϕ^{ext} . This interaction Hamiltonian density is

$$\delta h(1) = -\frac{1}{c} \mathbf{j}(1) \cdot \mathbf{A}^{\text{ext}}(1) + \frac{e}{2mc^2} \rho(1) [\mathbf{A}^{\text{ext}}(1)]^2 + \rho(1) \phi^{\text{ext}}(1), \quad (3.1)$$

where $\rho(1)$ and $\mathbf{j}(1)$ represent the charge density and current density operators in the absence of the applied field,¹⁶

$$\begin{aligned} \rho(1) &= e \sum_s \psi^\dagger(1) \psi(1), \\ \mathbf{j}(1) &= \frac{e}{2mi} (\nabla_1 - \nabla_1') \sum_s \psi^\dagger(1') \psi(1) \Big|_{1=1'} \\ &\quad - \frac{e}{2mc} \{ \rho(1), \mathbf{A}^{\text{int}}(1) \}. \end{aligned} \quad (3.2)$$

Here, $\mathbf{A}^{\text{int}}(1)$ is an operator which represents the vector potential which is induced by the particles within the system. The current operator in the presence of the external field is given by

$$\mathbf{J}(1) = \mathbf{j}(1) - \frac{e}{mc} \rho(1) \mathbf{A}^{\text{ext}}(1). \quad (3.3)$$

We wish to determine the expectation value of the current induced at time t by a weak electromagnetic field applied to a system in equilibrium at t_0 . Inasmuch as we are only interested in the linear response, we may employ first-order perturbation theory to derive

$$\begin{aligned} \langle \mathbf{J}_k(\mathbf{r}t) \rangle &= i \int_{t_0}^t dt' d\mathbf{r}' \langle [\mathbf{j}_k(\mathbf{r}t), \mathbf{j}_t(\mathbf{r}'t')] \rangle \frac{1}{c} \mathbf{A}_t^{\text{ext}}(\mathbf{r}'t') \\ &\quad - \frac{e\langle \rho \rangle}{mc} \mathbf{A}_k^{\text{ext}}(\mathbf{r}t) - i \int_{t_0}^t dt' d\mathbf{r}' \\ &\quad \times \langle [\mathbf{j}_k(\mathbf{r}t), \rho(\mathbf{r}'t')] \rangle \phi^{\text{ext}}(\mathbf{r}'t'). \end{aligned} \quad (3.4)$$

Assuming \mathbf{A}^{ext} and ϕ^{ext} vanish for times less than t_0 , we extend the lower limit from t_0 to $-\infty$.

Since the electromagnetic properties of the system were obtained in a specific gauge from $[\mathbf{j}, \mathbf{j}]$ in I, we anticipate a connection between $[\mathbf{j}, \mathbf{j}]$ and $[\rho, \mathbf{j}]$. Indeed, we expect the relation between them to be a consequence of current conservation or gauge invariance. We can

¹⁵ The suggestion that the superconducting transition is a Bose condensation phenomenon is one originally proposed by Blatt, Butler, and Schaforth.

¹⁶ The current operator is actually nonlocal in virtue of the momentum cutoffs in the simplified interaction. That interaction is, of course, justified because the cutoff appears inessentially in all calculations. In other words, the momentum-dependent terms are of order (Δ/ω_D) or smaller and may be freely ignored. In Eq. (3.3) the spin current has also been neglected but we shall consider it presently.

infer the form of this relation by comparing the values of $\langle \mathbf{J} \rangle$ determined in different gauges. Under the gauge transformation

$$\bar{\phi}^{\text{ext}}(\mathbf{r}t) = \phi^{\text{ext}}(\mathbf{r}t) - \frac{1}{c} \frac{\partial}{\partial t} \Lambda(\mathbf{r}t); \quad (3.5)$$

$$\bar{\mathbf{A}}^{\text{ext}}(\mathbf{r}t) = \mathbf{A}^{\text{ext}}(\mathbf{r}t) + \nabla \Lambda(\mathbf{r}t),$$

the expression (3.4) is altered by the amount

$$\begin{aligned} \Theta = & -\frac{e\langle \rho \rangle}{mc} \nabla_k \Lambda \\ & + i \int_{-\infty}^t dt' d\mathbf{r}' \langle [\mathbf{j}_k(\mathbf{r}t), \mathbf{j}_l(\mathbf{r}'t')] \rangle \frac{1}{c} \nabla_l \Lambda(\mathbf{r}'t') \\ & + i \int_{-\infty}^t dt' d\mathbf{r}' \langle [\mathbf{j}_k(\mathbf{r}t), \rho(\mathbf{r}'t')] \rangle \frac{1}{c} \frac{\partial}{\partial t'} \Lambda(\mathbf{r}'t'). \end{aligned} \quad (3.6)$$

If (3.4) is to be gauge invariant, Θ must vanish. After integrating by parts with respect to the time and taking into account the arbitrariness of Λ , we conclude that gauge invariance is maintained if and only if

$$\nabla_k \langle [\mathbf{j}_k(\mathbf{r}t), \mathbf{j}_l(\mathbf{r}'t')] \rangle = -(\partial/\partial t) \langle [\rho(\mathbf{r}t), \mathbf{j}_l(\mathbf{r}'t')] \rangle, \quad (3.7)$$

and

$$(-ie\langle \rho \rangle/m) \nabla_k \delta(\mathbf{r} - \mathbf{r}') = \langle [\mathbf{j}_k(\mathbf{r}t), \rho(\mathbf{r}'t)] \rangle. \quad (3.8)$$

Since Eq. (3.7) follows from the current conservation relation, and (3.8) is readily derived by the field commutation relations, gauge invariance is assured when exact correlation functions are employed. Furthermore, the gauge invariance of calculations based on approximate current correlation functions is preserved if and only if these approximate functions satisfy (3.7) and (3.8).

Before turning to actual calculations based upon approximate correlation functions, we introduce some additional definitions which permit us to express the condition (3.8) more conveniently, and to express (3.4) in terms of the electromagnetic fields when (3.7) and (3.8) are satisfied. We begin by writing (3.4) in the form

$$\begin{aligned} \langle \mathbf{J}_k(1) \rangle = & i \int d2 \langle [\mathbf{j}_k(1), \mathbf{j}_l(2)]_R \rangle \frac{1}{c} \mathbf{A}_l^{\text{ext}}(2) - \frac{e\langle \rho \rangle}{mc} \mathbf{A}_k^{\text{ext}}(1) \\ & - i \int d2 \langle [\mathbf{j}_k(1), \rho(2)]_R \rangle \phi^{\text{ext}}(2), \end{aligned} \quad (3.9)$$

where the retarded commutator is defined by

$$\langle [A(1), B(2)]_R \rangle = \eta_+(t_1 - t_2) \langle [A(1), B(2)] \rangle. \quad (3.10)$$

We also introduce an integral representation for the

current-current commutator

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}t), \mathbf{j}_l(\mathbf{r}'t')] \rangle \\ = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \omega \sigma_{kl}'(\mathbf{k}, \omega) \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')]. \end{aligned} \quad (3.11)$$

In a translationally and rotationally invariant system, symmetric under space and time inversions, the conductivity tensor $\sigma_{kl}'(\mathbf{k}, \omega)$ occurring in (3.11) may be expressed in the form [cf. I, Eq. (4.37)]

$$\begin{aligned} \sigma_{kl}'(\mathbf{k}, \omega) = & \sigma'^L(k^2\omega^2) (\mathbf{k}_k \mathbf{k}_l / k^2) \\ & + \sigma'^T(k^2\omega^2) [\delta_{kl} - (\mathbf{k}_k \mathbf{k}_l / k^2)], \end{aligned} \quad (3.12)$$

where L and T indicate longitudinal and transverse parts. We may write the Fourier transform of the commutators appearing in (3.9) in terms of the representation (3.11). In particular, the transform with respect to the time difference variable is given by

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}), \mathbf{j}_l(\mathbf{r}')]_R \rangle(\omega) \\ = \int_{-\infty}^0 dt e^{-i\omega t} \int \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\omega'}{\pi} \omega' \sigma_{kl}'(\mathbf{k}, \omega') \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + i\omega' t + \epsilon t]. \end{aligned} \quad (3.13)$$

On carrying out the time integration we find

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}), \mathbf{j}_l(\mathbf{r}')]_R \rangle(\omega) \\ = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} [\omega \sigma_{kl}'(\mathbf{k}, \omega) + i\nu_{kl}'(\mathbf{k}, \omega)], \end{aligned} \quad (3.14)$$

where $\nu_{kl}'(\mathbf{k}, \omega)$ is defined by

$$\nu_{kl}'(\mathbf{k}, \omega) = -\frac{2}{\pi} \int_0^\infty d\omega' P \frac{\omega'^2}{\omega'^2 - \omega^2} \sigma_{kl}'(\mathbf{k}, \omega'), \quad (3.15)$$

and

$$\begin{aligned} \nu_{kl}'(\mathbf{k}, \omega) = & \nu'^L(k^2\omega^2) (\mathbf{k}_k \mathbf{k}_l / k^2) \\ & + \nu'^T(k^2\omega^2) [\delta_{kl} - (\mathbf{k}_k \mathbf{k}_l / k^2)]. \end{aligned} \quad (3.16)$$

To determine $\langle [\mathbf{j}(\mathbf{r}), \rho(\mathbf{r}')]_R \rangle(\omega)$, we invoke the relation (3.7) and note that the divergence operation projects out the longitudinal part of σ_{kl}' . We therefore write

$$\begin{aligned} \left\langle \left[\mathbf{j}_k(\mathbf{r}t), \frac{\partial \rho}{\partial t'}(\mathbf{r}'t') \right] \right\rangle \\ = -\nabla_k \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \omega \sigma'^L(k^2\omega^2) \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')], \end{aligned} \quad (3.17)$$

and integrate with respect to time, obtaining

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}t), \rho(\mathbf{r}'t')] \rangle \\ = i\nabla_k' \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \sigma'^L(k^2\omega^2) \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')]. \end{aligned} \quad (3.18)$$

The quantity $\langle [\mathbf{j}_k(\mathbf{r}), \rho(\mathbf{r}')]_R \rangle(\omega)$ may now be written in the form

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}), \rho(\mathbf{r}')]_R \rangle(\omega) \\ = i\nabla_k' \int_{-\infty}^0 dt e^{-i\omega t} \int \frac{d\omega'}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \\ \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + i\omega't + \epsilon t] \sigma'^L(k^2\omega'^2). \end{aligned} \quad (3.19)$$

On performing the time integration, we find

$$\begin{aligned} \langle [\mathbf{j}_k(\mathbf{r}), \rho(\mathbf{r}')]_R \rangle(\omega) \\ = i\nabla_k' \int \frac{d\mathbf{k}}{(2\pi)^3} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \left\{ \sigma'^L(k^2\omega^2) \right. \\ \left. - \frac{1}{i\omega} \left[\nu'^L(k^2\omega^2) + \frac{2}{\pi} \int_0^\infty d\omega' \sigma'^L(k^2\omega'^2) \right] \right\}. \end{aligned} \quad (3.20)$$

We now substitute (3.14) and (3.20) into (3.9) and take the Fourier transform of the resulting equation, obtaining

$$\begin{aligned} \langle \mathbf{J}_k(\mathbf{k}, \omega) \rangle \\ = \frac{e\langle \rho \rangle}{mc} \mathbf{A}_k^{\text{ext}}(\mathbf{k}, \omega) - (\nu_{kl}' - i\omega\sigma_{kl}') \frac{1}{c} \mathbf{A}_l^{\text{ext}}(\mathbf{k}, \omega) \\ + \left[\frac{2}{\pi} \frac{1}{i\omega} \int_0^\infty d\omega' \sigma'^L(k^2\omega'^2) + \frac{\nu'^L(k^2\omega^2)}{i\omega} - \sigma'^L(k^2\omega^2) \right] \\ \times i\mathbf{k}_k \phi^{\text{ext}}(\mathbf{k}, \omega). \end{aligned} \quad (3.21)$$

Under the gauge transformation (3.5) the right-hand side of Eq. (3.21) is changed by Θ where

$$\Theta = \left[-\frac{e\langle \rho \rangle}{mc} + \frac{2}{\pi c} \int_0^\infty d\omega' \sigma'^L(k^2\omega'^2) \right] i\mathbf{k}_k \Lambda. \quad (3.22)$$

Hence, if Eq. (3.21) is to be gauge invariant, Θ must vanish, that is, the longitudinal sum rule,

$$\frac{2}{\pi} \int_0^\infty d\omega' \sigma'^L(k^2\omega'^2) = e\langle \rho \rangle / m, \quad (3.23)$$

must be satisfied. The right-hand side of Eq. (3.21) may then be expressed in terms of the externally applied

electric field

$$\langle \mathbf{J}_k(\mathbf{k}, \omega) \rangle = \left\{ \sigma_{kl}' - \frac{1}{i\omega} \left[\nu_{kl}' + \delta_{kl} \frac{e\langle \rho \rangle}{m} \right] \right\} \mathbf{E}_l^{\text{ext}}(\mathbf{k}, \omega), \quad (3.24)$$

where

$$\mathbf{E}_l^{\text{ext}}(\mathbf{k}, \omega) = (i\omega/c) \mathbf{A}_l^{\text{ext}}(\mathbf{k}, \omega) - i\mathbf{k}_l \phi^{\text{ext}}(\mathbf{k}, \omega). \quad (3.25)$$

We summarize as follows. An approximation to the correlation functions of a many-particle system describes its electromagnetic properties in a gauge-invariant manner if, and only if, the approximation satisfies the sum rule (3.23) and the particle-conservation statement (3.7). Since (3.23) is a direct consequence of the equal-time commutation relation (3.8), a sufficient condition for gauge invariance is that the approximate correlation functions satisfy (3.7) and (3.8).

Although it is gauge invariant, (3.24) does not characterize the electromagnetic transport properties of the system in the conventional manner. Ordinarily, the conductivity of a system is not defined as the coefficient which relates the induced current to the externally applied field, but as the coefficient relating the induced current to the total electric field in the system. To convert Eq. (3.24) into a relation between the induced current and the total field in the system, we write it in the form

$$\langle \mathbf{J}_k \rangle = -i\omega \tilde{\alpha}_{kl}' \mathbf{E}_l^{\text{ext}} \equiv -i\omega(\epsilon' - 1)_{kl} \mathbf{E}_l^{\text{ext}}, \quad (3.26)$$

where $\tilde{\alpha}_{kl}'$ is a complex polarizability tensor defined by

$$\omega^2 \tilde{\alpha}_{kl}' = -\nu_{kl}' + \delta_{kl} (e\langle \rho \rangle / m) + i\omega\sigma_{kl}'. \quad (3.27)$$

We would like to determine the coefficient $\tilde{\alpha}_{kl}$ which appears in the relation

$$\langle \mathbf{J}_k \rangle = -i\omega \tilde{\alpha}_{kl} \langle \mathbf{E}_l^{\text{tot}} \rangle \equiv -i\omega(\epsilon - 1)_{kl} \langle \mathbf{E}_l^{\text{tot}} \rangle, \quad (3.28)$$

where $\langle \mathbf{E}^{\text{tot}} \rangle$, the total electric field in the system, equals $\mathbf{E}^{\text{ext}} + \langle \mathbf{E}^{\text{int}} \rangle$.

By using the Maxwell equation

$$\nabla \cdot \mathbf{E}^{\text{int}} = \rho \quad (3.29)$$

and the current conservation equation for the induced charge

$$\nabla \cdot \mathbf{J} + (\partial/\partial t)\rho = 0, \quad (3.30)$$

we obtain between the longitudinal parts of the two polarizabilities defined above, the relation

$$\tilde{\alpha}^L = \tilde{\alpha}'^L [1 - \tilde{\alpha}'^L]^{-1}; \quad \epsilon^L = (\epsilon'^L)^{-1}. \quad (3.31)$$

Similarly, by using

$$c^2 \nabla \times (\nabla \times \mathbf{E}^{\text{tot}}) + (\partial^2 \mathbf{E}^{\text{tot}} / \partial t^2) = -\partial \mathbf{J} / \partial t, \quad (3.32)$$

we learn that the transverse parts of the two polarizabilities are connected by

$$\tilde{\alpha}^T = \tilde{\alpha}'^T [\omega^2 - c^2 k^2] [\omega^2 - c^2 k^2 - \omega^2 \tilde{\alpha}'^T]^{-1}. \quad (3.33)$$

The quantities α' and α , which describe the response

to an externally applied electric field and to the total electric field, are very different. The polarizability α' is directly connected with a current correlation function of the system, while α is a derived quantity. However, in most discussions of electrical transport α is the more natural quantity to discuss. For example, if we write

$$\tilde{\alpha}_{kl} = \alpha_{kl} + i\sigma_{kl}/\omega; \quad \epsilon_{kl} = \epsilon_{kl}^{(1)} + i\epsilon_{kl}^{(2)}, \quad (3.34)$$

then, the longitudinal part of $\sigma_{kl} = \omega\epsilon_{kl}^{(2)}$ reduces in a low-frequency, low wave number limit to the dc electrical conductivity. Furthermore, the quantity $\tilde{\alpha}^T$ is measured by thin film absorption experiments at low frequencies. On the other hand, the polarizability α' contains a pole corresponding to plasma oscillations which is absent in α . Thus, in the discussion of plasma oscillations, it is more natural to work with α' .

To compute α we must include the electromagnetic interactions between the particles in the Hamiltonian of the system. Their inclusion considerably complicates all calculations. Thus, following previous authors, we shall make the assumption that the complex polarizability tensor α , which represents the response to the total electromagnetic field, may be computed by evaluating the response to an external electromagnetic field for a system in which the long range part of the interparticle electromagnetic interaction is neglected. In other words, we assume that α can be approximately evaluated by employing Eq. (3.11),

$$\langle [\mathbf{j}_k(1), \mathbf{j}_l(2)] \rangle = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \omega \sigma_{kl}(\mathbf{k}, \omega) \times \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) - i\omega(t_1 - t_2)], \quad (3.35)$$

where the expectation value is to be computed in a system for which the Hamiltonian includes the non-electromagnetic interaction between particles but only the short-range (screened) part of the electromagnetic interaction.¹⁷

This assumption is connected with the random phase approximation.¹⁸ Physically, it is based upon the notion that the electromagnetic forces are so long-ranged that a particle responds to the electric field created by other

¹⁷ In order to obtain the pole at the plasma frequency in σ' , we then use (3.31) on the approximation to $\tilde{\alpha}$. At high frequencies, $\omega\sigma$ becomes exceedingly small and α approaches $-ne^2/m\omega^2$. Thus, at very high frequencies, σ' is approximately given by $(\pi ne^2/2m) \times \delta(\omega - \omega_p)$, where $\omega_p = (ne^2/m)^{1/2}$ is the plasma frequency. Since the plasma frequency is much larger than Δ or β^{-1} in a superconductor, this form for σ' is quite accurate. Moreover, the contribution to σ' at the plasma frequency effectively exhausts the sum rule so that the low-frequency contribution to σ' must be quite small.

¹⁸ P. Nozières and D. Pines, Phys. Rev. **113**, 1254 (1959), where references to earlier articles are also given. It should perhaps be pointed out that these authors proved that ϵ' satisfied a dispersion relation by invoking the mathematical properties of the correlation function $(\epsilon')^{-1}$. Equation (3.31) indicates the physical significance of this fact, that is, that ϵ' also describes the causal linear response to the total field. Their mathematical sum rule for $\text{Im}\epsilon'$ is just the physical sum rule for the experimental longitudinal conductivity.

particles in the same manner as it responds to an externally applied field.¹⁸

Furthermore, the assumption that α' may be computed by computing α for a system with only short-range interactions and then using Eqs. (3.31) and (3.33) seems to lead to no mathematical inconsistencies. There are two requirements on the consistency of this calculational procedure. The first is that the function α' computed in this manner must satisfy Kramers-Kronig relations, that is, α' must have no poles in the upper half of the complex frequency plane. The second is that the longitudinal part of σ' which emerges from this calculation must satisfy the sum rule (3.23). Fortunately, this type of computation must always lead to an $\tilde{\alpha}'$ which satisfies both conditions. One can easily show that if $\tilde{\alpha}$ satisfies these conditions, $\tilde{\alpha}'$ must also satisfy them. Thus, the "random phase approximation" calculation procedure is internally consistent and physically reasonable. In the calculations which follow, we shall employ it. That is to say, we shall compute the current correlation function for a system in which there is only a short-range interaction. In fact, as before, we shall choose the potential to be a delta function of space and time in which the momentum components near the edge of the Fermi sea are projected out.

Even when our problem is reduced to a calculation of current correlation functions in the presence of short-ranged forces, however, we must ensure that the approximations we employ lead to correlation functions consistent with particle conservation and the associated longitudinal sum rule on σ^L . Consequently, we shall devote part C of this section to the discussion of criteria which guarantee that a particular approximation leads to gauge-invariant results.

B. Magnetic Properties

Before turning to these questions of gauge invariance, we consider the electromagnetic properties connected with the transverse part of the current-correlation function. We shall show subsequently that the modifications that bring about gauge invariance do not substantially alter this transverse response.

In I the manipulations which related the retarded commutator to the time-ordered product were carried out, and it was shown that

$$\begin{aligned} \omega \sigma_{kl}(\mathbf{k}, \omega) \coth \frac{1}{2}\beta\omega + i\nu_{kl}(\mathbf{k}, \omega) \\ = \frac{e^2}{(2m)^2} \sum_{s_1 s_2} \int d\mathbf{r}_1 dt_1 \exp[-i\mathbf{k} \cdot \mathbf{r}_1 + i\omega t_1] \\ \times (\nabla_1 - \nabla_1')_k (\nabla_2 - \nabla_2')_l G^{s_1 s_2}(12; 1'2'), \end{aligned} \quad (3.36)$$

with the limits $\mathbf{r}_1' \rightarrow \mathbf{r}_1$, $t_1' \rightarrow t_1^+$, $\mathbf{r}_2 \rightarrow 0$, $\mathbf{r}_2' \rightarrow 0$, $t_2 \rightarrow 0$, $t_2' \rightarrow 0^+$. It is convenient to evaluate separately the contributions to (3.36) arising from G^{++} and G^{+-} . We denote them by σ_{kl}^{++} (and ν_{kl}^{++}) and σ_{kl}^{+-} (and ν_{kl}^{+-}), respectively. This division is useful since the

commutator $\langle [\mathbf{j}_k^s(1), \mathbf{j}_{k'}^{s'}(2)] \rangle$ is related to $\frac{1}{2}\sigma_{kl}^{ss'}$ in the same manner as $\langle [\mathbf{j}_k(1), \mathbf{j}_l(2)] \rangle$ is related to σ_{kl} . Indeed, the kernel $\frac{1}{2}\omega\sigma_{kl}^{+-}(\mathbf{k}, \omega)$ of the Fourier transform of $\langle [\mathbf{j}_k^+(1), \mathbf{j}_l^-(2)] \rangle$ also consists of two real functions $\sigma^{L+-}(k^2\omega^2)$ and $\sigma^{T+-}(k^2\omega^2)$. The reality of these functions is a consequence of rotational invariance, time reversibility, and the Hermitian character of the operators \mathbf{j}^+ and \mathbf{j}^- . It is simpler, however, to demonstrate the reality by observing that

$$\langle [\mathbf{j}^+(1), \mathbf{j}^-(2)] \rangle = \frac{1}{2} \langle [\mathbf{j}(1), \mathbf{j}(2)] \rangle - \langle [\mathbf{j}^+(1), \mathbf{j}^+(2)] \rangle. \quad (3.37)$$

This form enables us also to conclude that $\sigma^{L++}(k^2\omega^2)$ and $\sigma^{L++}(k^2\omega^2) - \sigma^{L+-}(k^2\omega^2)$ are positive definite.

Direct substitution of (2.9) and (2.30) into (3.36) yields the expressions

$$\begin{aligned} \omega\sigma^{T++}(k^2\omega^2) \coth \frac{1}{2}\beta\omega + i\nu^{T++}(k^2\omega^2) \\ = -\frac{e^2}{m^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \left[k'^2 - \frac{(\mathbf{k}' \cdot \mathbf{k})^2}{k^2} \right] \\ \times G(\mathbf{k}_+, \omega_+) G(\mathbf{k}_-, \omega_-), \end{aligned} \quad (3.38)$$

and

$$\begin{aligned} \omega\sigma^{T+-}(k^2\omega^2) \coth \frac{1}{2}\beta\omega + i\nu^{T+-}(k^2\omega^2) \\ = -\frac{e^2}{m^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \left[k'^2 - \frac{(\mathbf{k}' \cdot \mathbf{k})^2}{k^2} \right] \\ \times F(\mathbf{k}_+, \omega_+) F(\mathbf{k}_-, \omega_-), \end{aligned} \quad (3.39)$$

where

$$\mathbf{k}_{\pm} = \mathbf{k}' \pm \frac{1}{2}\mathbf{k} \quad \text{and} \quad \omega_{\pm} = \omega' \pm \frac{1}{2}\omega.$$

In Appendix I these integrals are evaluated in some limiting cases. In particular, it is shown that in the static limit the polarizability reduces to

$$\begin{aligned} \nu^{T++}(k^2 0) &= (ne^2/m) [\frac{1}{2}S_T(k^2) - 1], \\ \nu^{T+-}(k^2 0) &= (ne^2/m) \frac{1}{2}S_T(k^2), \end{aligned} \quad (3.40)$$

or

$$\lim_{\omega \rightarrow 0} \alpha^T(k^2\omega^2) = -\frac{ne^2}{m\omega^2} S_T(k^2). \quad (3.41)$$

The function $S_T(k^2)$ may be expressed in the form

$$S_T(k^2) = \frac{3}{2}S_T^{(0)}(k^2) - \frac{1}{2}S_T^{(2)}(k^2), \quad (3.42)$$

where

$$\begin{aligned} S_T^{(0)}(k^2) &= \frac{\pi^2}{2} \frac{\Delta}{kv_F} \tanh \frac{1}{2}\beta\Delta \\ &+ \frac{\Delta^2}{kv_F} \int_0^\infty \frac{d\epsilon}{\epsilon E} \tanh \frac{1}{2}\beta E \ln \left| \frac{\epsilon + \frac{1}{2}kv_F}{\epsilon - \frac{1}{2}kv_F} \right|; \\ S_T^{(2)}(k^2) &= \frac{3\Delta^2}{kv_F} \int_0^\infty \frac{d\epsilon}{\epsilon E} \tanh \frac{1}{2}\beta E \\ &\times \left[-\frac{4\epsilon}{kv_F} + 4 \left(\frac{\epsilon}{kv_F} \right)^2 \ln \left| \frac{\epsilon + \frac{1}{2}kv_F}{\epsilon - \frac{1}{2}kv_F} \right| \right]. \end{aligned} \quad (3.43)$$

The spin susceptibility, $\chi_{sp}(k^2 0)$, in the BCS approximation involves a similar computation. In particular it reduces to

$$\chi_{sp}(k^2 0) = (\mu_e^2 m p_F / \pi^2) [1 - S_T^{(0)}(k^2)], \quad (3.44)$$

where μ_e is the magnetic moment of the electron. The quantity $S_T^{(0)}(k^2)$ takes the value 1 as k approaches zero at vanishing temperature. It vanishes and χ takes on the free-electron Pauli values as $k \rightarrow \infty$ or as $\Delta \rightarrow 0$. Therefore $S_T^{(0)}$ may be regarded as the fraction of superconducting electrons in a magnetic field of wave number k at temperature T when emphasis is put on spin phenomena. The quantity $S_T(k^2)$ has similar limiting values and may be regarded as the fraction of superconducting electrons of wave number k when the emphasis is on motional current properties. For small wave numbers, the functions S_T , $S_T^{(0)}$, and $S_T^{(2)}$ agree and define the fraction of superconducting electrons appropriate to a two-fluid model. These functions differ considerably from another quantity, the fraction of condensate, which appeared in the analog of (2.48) and could also be called the fraction of superconducting electrons. The latter is much smaller than one, even in the low-wavelength limit, and is similar to the functions S only in that it vanishes at $T = T_c$.

When we insert the derived constitutive equation for the superconductor into Ampere's law for a transverse field, neglecting the contribution of the spin current, we obtain

$$c\mathbf{k} \times \mathbf{B} + i\omega \mathbf{E}^T = \mathbf{J}^T + (\mathbf{J}^{\text{ext}})^T, \quad (3.45)$$

where \mathbf{J}^{ext} represents the free external currents which produce the magnetic field. From Faraday's law and the solenoidal character of \mathbf{B} we then obtain

$$\begin{aligned} [\omega^2 - c^2 k^2 + i\omega\sigma^T(k^2\omega^2) + \omega^2\alpha^T(k^2\omega^2)]\mathbf{B}(\mathbf{k}, \omega) \\ = -i\mathbf{k}c \times \mathbf{J}^{\text{ext}}(\mathbf{k}, \omega). \end{aligned} \quad (3.46)$$

The transverse electric field satisfies a similar equation. In a static magnetic field, (3.46) becomes

$$[k^2 + \kappa^2(k^2)]\mathbf{B}(\mathbf{k}) = i\mathbf{k}c \times \mathbf{J}^{\text{ext}}/c, \quad (3.47)$$

where $\kappa^2(k^2)$ is given by

$$c^2\kappa^2(k^2) = -\lim_{\omega \rightarrow 0} \omega^2\alpha^T(k^2\omega^2) = (ne^2/m)S_T(k^2). \quad (3.48)$$

It follows from (3.47) that an external point source gives rise to a magnetic field which falls off exponentially in a characteristic distance $\lambda = ik_0^{-1}$, where k_0 is determined by the solution to $k_0^2 + \kappa^2(k_0) = 0$. For values of $k \ll \xi_T^{-1} \equiv \pi\Delta_T/V_F$, Eq. (3.48) reduces to $\lambda_T^2 = (ne^2/mc^2) \times S_T(0)$. This limit, the London limit, leads to an attenuation length, consistent with $k\xi_T \ll 1$ when $\lambda_T \ll \xi_T$. Correspondingly, if $k\xi_T \ll 1$, Eq. (3.41) reduces to

$$\kappa^2 = \frac{3ne^2}{mc^2} \frac{\pi^2}{4} \frac{\Delta}{kv_F} \tanh \frac{1}{2}\beta\Delta. \quad (3.49)$$

The attenuation distance for a point source is then

given by

$$\lambda_T = \left(\frac{mc^2}{ne^2} \frac{4\xi_T}{3\pi} \coth \frac{\beta\Delta_T}{2} \right)^{\frac{1}{3}}, \quad (3.50)$$

which is consistent with $k\xi_T \gg 1$ whenever $\lambda_T \gg \xi_T$. The latter limit, the Pippard limit, is typical of superconductors except near the critical temperature. In this rapid attenuation limit, the temperature variation of the penetration depth, determined from the leading term in (3.50), is

$$\lambda_T/\lambda_0 = [\Delta_0/\Delta_T \tanh \frac{1}{2}\beta\Delta_T]^{\frac{1}{3}}. \quad (3.51)$$

The penetration depth for a more complicated field source differs from (3.50) by a factor of order unity. The determination of this factor requires solution of the electromagnetic problem which specifies the source configuration in question.¹⁹

C. Criteria for a Gauge-Invariant Approximation

For the discussion of gauge-invariant approximations it is useful to recast the charge-conservation correlation in an alternative form. We begin by introducing an equation sufficient to guarantee the gauge invariance of the current-current correlation function:

$$\begin{aligned} [G_0^{-1}(1) - G_0^{-1}(1')] L^{s_1 s_2}(12; 1'2')|_{1' \rightarrow 1} \\ = \delta_{s_1 s_2} [-\delta(1-2')G(2-1') \\ + \delta(2-1)G(1-2')]. \end{aligned} \quad (3.52)$$

If we apply the operator $(-ie^2/2m)(\nabla_2 - \nabla_{2'})$ to this equation, set 2 equal to 2', and use the definitions (3.2) of the charge density and current density operators neglecting the term involving \mathbf{A}^{int} , we arrive at the statement

$$\begin{aligned} \frac{\partial}{\partial t_1} \langle (\rho(1)\mathbf{j}(2))_+ \rangle + \nabla_1 \cdot \langle (\mathbf{j}(1)\mathbf{j}(2))_+ \rangle = \frac{ne^2}{m} \frac{1}{i} \\ \times \nabla_1 \delta(1-2). \end{aligned} \quad (3.53)$$

The discontinuity in (3.53) reproduces (3.8), from which we derive the sum rule on the longitudinal conductivity; the continuous vanishing part of (3.53) leads to the matrix element (3.7) of the current conservation law. Thus, if an approximate two-particle correlation function satisfies (3.52), it must predict electromagnetic properties gauge invariantly.

We are therefore led to search for approximations which obey (3.52). We begin by noting that (3.52) emerges from the exact equation of motion,

$$\begin{aligned} G_0^{-1}(1)G_2^{s_1 s_2}(12; 1'2') \\ = \delta(1-1')G(2-2') - \delta_{s_1 s_2} \delta(1-2')G(2-1') \\ - i \int v(13) \sum_{s_3} G_3^{s_1 s_2 s_3}(123; 1'2'3') d3, \end{aligned} \quad (2.4)$$

and the time-reversed statement,

$$\begin{aligned} G_2^{s_1 s_2}(12; 1'2')G_0^{-1}(1') \\ = \delta(1-1')G(2-2') - \delta_{s_1 s_2} \delta(2-1')G(1-2') \\ - i \int v(1'3) \sum_{s_3} G_3^{s_1 s_2 s_3}(123; 1'2'3'), \end{aligned} \quad (2.4')$$

when the points 1 and 1' are identified and (2.4') subtracted from (2.4).

In order to find an approximation for the two-particle correlation function, it is necessary to express G_3 in terms of the one- and two-particle Green's functions. To lowest order, this is accomplished by the expansion procedure suggested in I. A better approximation involves solving an equation for G_3 . In any event, G_3 is approximated by some functional of G_1 and G_2 . This approximate expression for G_3 is inserted in (2.4) or (2.4'), which is then solved for the two-particle correlation function.

We can guarantee that such a procedure yields a function G_2 which satisfies (2.36) by imposing two symmetry requirements:

- (a) The approximation for G_3 in the right-hand side of (2.4) must be symmetric under interchange of all n and n' indices.
- (b) The two-particle correlation function derived from G_3 must have the same symmetry.

That is to say, the approximation for G_3 as a functional of G_2 and G_1 must remain invariant under the transposition $G_3(123; 1'2'3') \rightarrow G_3(1'2'3'; 123)$ and simultaneous transposition of all indices of the functions G_1 and G_2 . Similarly, the equation for $G_2(12; 1'2')$ expressed as a functional of $G_1(a, a')$ must be invariant under the transformation $G_2(12; 1'2') \rightarrow G_2(1'2'; 12)$ and $G_1(a, a') \rightarrow G_1(a', a)$. If the requirements (a) and (b) are satisfied, then, when G_3 is approximated in terms of G_1 's and G_2 's in (2.4), the equation (2.4') follows with the same approximation for G_3 . The gauge invariance of the approximate two-particle correlation function can therefore be deduced as it is for the exact correlation function, by subtracting (2.4) from (2.4').

Let us apply these criteria to the approximate Green's functions which were derived in Sec. 2. We first observe that Eq. (3.52) is not satisfied by either approximation (2.9) for L^{++} nor approximation (2.31) for L^{+-} . In fact, we see that

$$\begin{aligned} [G_0^{-1}(1) - G_0^{-1}(1')] L^{++}(12; 1'2')|_{1=1'} \\ = -\delta(1-2')G(2-1) + \delta(2-1)G(1-2') \\ + \Delta F(1-2')G(2-1) - \Delta F(2-1)G(1-2'); \end{aligned} \quad (3.54)$$

$$\begin{aligned} [G_0^{-1}(1) - G_0^{-1}(1')] L^{+-}(12; 1'2')|_{1=1'} \\ = \Delta F(1-2')G(2-1) - \Delta F(2-1)G(1-2'). \end{aligned}$$

By adding the two equations (3.54) we deduce that the correlation functions of Sec. 2 do not conserve the total

¹⁹ J. R. Schrieffer, Phys. Rev. **106**, 47 (1957); R. M. May and M. R. Schafroth, Proc. Phys. Soc. (London) **74**, 153 (1959).

number of particles. By subtracting these equations, we find that the BCS approximation conserves total spin.

This leads us naturally to ask where we erred when we derived the BCS correlation functions. The function L satisfies criterion (b) as we can verify by inspection of (2.9) or (2.31). However, it does not satisfy criterion (a). In determining L^{++} , we used the approximation

$$\begin{aligned} G_3^{+-}(123; 1'2'3')|_{3=1} \\ = G(3-3^+)G_2^{++}(12; 1'2') \\ + G(2-2')L^{+-}(13; 1'3) \\ - G(2-1')L^{+-}(13; 2'3)|_{3=1}, \end{aligned} \quad (3.55)$$

while in the determination of L^{+-} we assumed

$$\begin{aligned} G^{+-}(123; 1'2'3')|_{3=1} \\ = G(3-3^+)G_2^{+-}(12; 1'2') \\ + G(2-2')L^{+-}(13; 1'3) \\ - G(2-3)L^{+-}(13; 1'2')|_{3=1}. \end{aligned} \quad (3.56)$$

The first two terms on the right-hand side of (3.55) and (3.56) are indeed symmetric. The quantity $L^{+-}(13; 1'3)$ is symmetric since

$$F(0)F(1-1') = F(0)F(1'-1).$$

On the other hand, the last term on the right-hand side of each of these equations is not symmetric, and consequently the approximation procedure does not satisfy criterion (a). We might try to improve the approximation by including more terms in an expansion of G_3 . For example, we could satisfy criterion (a) by adding the term $-G(1-2')L^{+-}(12; 1'1)$ to the right-hand side of (3.55) and the term $-G(3-2')L^{+-}(12; 1'3)$ to the right-hand side of (3.56). However, the resulting equations for $L^{++}(12; 1'2')$ and $L^{+-}(12; 1'2')$ are very difficult to solve except by considering the terms we have just appended to be perturbations. If one does consider these terms to be perturbations, the resulting functions L^{++} and L^{+-} do not satisfy criterion (b). We have therefore reached an impasse.

4. IMPROVED DENSITY CORRELATION FUNCTIONS

There are two approaches we might try at this point: We might attempt to reformulate our approximation procedure entirely or we might attempt to obtain a better approximation for G_3 by writing an equation for G_3 in terms of G_4 and factoring G_4 . In this paper, we shall derive gauge-invariant expressions for the two-particle correlation functions by the former course, using a very convenient procedure suggested by Nambu.²⁰ However, we shall first verbally describe how these results would emerge from the latter course, since factorization of G_4 provides an alternative, but cumbersome, method for deriving the results we obtain more compactly below.

If we write an equation for G_3 in terms of G_4 and factor

G_4 , we find that $G_3^{+-}(123; 1'2'3')$ does not vanish as the points 1 and 3 become infinitely far removed from all the other points in the correlation function. In fact, we find that in this limit G_3 approaches $F(1-3)$ times a function $E(2; 1'2'3')$. The G_3 equation enables us to write an integral equation for E in which there is an inhomogeneous term which involves the two-particle correlation function. Similarly, when we use Eq. (2.4) to write an equation for the two-particle correlation function, we find that L is in turn determined by E . We consequently arrive at a set of simultaneous equations for L and E (which also contain the adjoint of E , a matrix element of three creation operators and one annihilation operator). These equations are similar to the ones proposed by Anderson.⁵ Their approximate nonperturbative solution leads to an equation for L which satisfies criteria (a) and (b) and is therefore gauge invariant.

We may briefly describe the physical basis of these manipulations. The two-particle correlation function $L(12; 12)$ is related to the change in the density of particles at the point 1 caused by a density fluctuation at the point 2. The function $iVE(2; 1'2'1')$ is connected to the gap energy $iVF(0)$ in the same way as $L(12; 12)$ is connected to the density $-iG(0-)$. Thus, $E(2; 1'2'1')$ may be said to describe a change in the local value of the gap energy, caused by a density fluctuation. In a normal system, equilibrium is restored after a density fluctuation because local changes in the chemical potential produce forces which restore equilibrium. Moreover, the low-frequency low-wave-number Fourier transform of $L(12; 12)$, the partial derivative of the density with respect to the chemical potential at constant temperature, characterizes the restoring force. In a superconductor, density fluctuations produce local changes in the gap energy which in turn produce forces that restore equilibrium. Since the low-frequency Fourier transform of $-iVE(2; 1'2'1')$ represents the partial derivative of the gap energy with respect to the chemical potential at constant temperature, it characterizes restoration of equilibrium in a superconductor after a density fluctuation. The mathematical complexity which leads to gauge invariance may therefore be described physically through the inclusion of an additional physical effect, the variation in energy gap with local density variation, which restores the system to equilibrium. In a two-component system, where the momentum of a single component is not conserved, equilibrium is restored by diffusion as well as sound propagation. We shall not discuss this complication here, but merely state that an approximate treatment of the phonons appears to lead to a gauge-invariant density correlation function in which a diffusion pole plays the role that a sound-wave pole will play in the present discussion.

The procedure outlined above—writing a G_3 in terms of a G_4 , finding that the G_3 contains terms involving a four-point function E , and finally solving simultaneous equations for E and L —is rather long and involved. In

²⁰ Y. Nambu, Phys. Rev. 117, 648 (1960).

order to derive these results more compactly, let us examine some implications of the existence of the function E .

We first observe that we should expect $G_3(123; 1'2'3')$ to contain an important term which has the form $F(1-3)E(2; 1'2'3')$. The two-particle correlation function contains a term of the form $F(1-2)F(1'-2')$ because there exists a set of anomalously large matrix elements between typical states of N_+ particles with spin up, N_- particles with spin down, total energy E , and total momentum P and states which have N_++1 particles with spin up, N_-+1 particles with spin down, total energy $E+2E_F$, and total momentum P . If these matrix elements are large, they should also have an effect on $G_3^{+-}(123; 1'2'3')$. In particular, if we expand G_3 in terms of a complete set of states containing matrix elements of two creation operators 1 and 3 and of the remainder of the operators in G_3 , the unusually large matrix elements are large, they should also have an effect on $G_3^{+-}(123; 1'2'3')$. In particular, if we expand G_3 in terms of a complete set of states containing matrix elements of identical total momentum, total number of particles differing by 2, and total energy differing by $2E_F$. We can take into account the term FE in G_3 by extending the factorization procedure outlined in I to include the fact that a better approximation for G_3 than the factorization (2.5) would include a series of terms of the form FE as well as the series of terms GL . Similarly, we can generalize the factorization approximations for all the higher-order Green's functions.

Furthermore, we have some experience to indicate that a good approximation procedure would involve treating all functions with the same number of indices on the same footing. Thus, we originally solved equations for F and G simultaneously, and, as we have just outlined, it is necessary to solve the equations for E and L at the same time. We may also infer that higher-order approximations would involve solving equations for various different types of six-point functions, including ones which involved matrix elements of three creation and three annihilation operators, two creation and four annihilation operators, six annihilation operators, and so forth.

Computationally, it is rather cumbersome to use the conventional Green's function language, include the extra factorizations, and treat all n -point functions alike. It is much more convenient to generalize the Green's functions to include in a matrix sense all the different possible functions with a given number of coordinate indices. Such a generalization is conveniently accomplished with the aid of a procedure suggested by Nambu.

Let us consider matrix creation and annihilation operators of the form

$$\Psi(1) = \begin{bmatrix} \psi(1+) \\ a(1)\psi^\dagger(1-) \end{bmatrix}, \quad (4.1)$$

$$\Psi^\dagger(1') = [\psi^\dagger(1'+) \quad a^\dagger(1')\psi(1'-)],$$

where a is an operator which destroys two particles of equal and opposite momentum in a state and reduces its energy by $2E_F$. In particular, we choose for a

$$a(t) = C \int d\mathbf{r} \psi(\mathbf{r}t+) \psi(\mathbf{r}t-), \quad (4.2)$$

where C is defined as a real number such that

$$\langle aa^\dagger \rangle = 1. \quad (4.3)$$

If we make use of the BCS type solution to evaluate C , we find that C approaches zero as the inverse volume of the system. As a result, the operator a is of order unity and projects out the anomalously large matrix elements which were discussed above.

We define a matrix one-particle Green's function by using a natural generalization of the ordinary definition of the one-particle Green's function:

$$\mathcal{G}(1-1') = -i\epsilon(1-1') \langle (\Psi(1)\Psi^\dagger(1'))_+ \rangle. \quad (4.4)$$

When we apply the definition of F and G we find that this matrix Green's function is

$$\mathcal{G}(1-1') = \begin{pmatrix} G(1-1') & F(1'-1) \\ F(1-1') & -G(1'-1) \end{pmatrix}, \quad (4.5)$$

and its Fourier transform is

$$\mathcal{G}(p) = \begin{pmatrix} G(p) & F(-p) \\ F(p) & -G(-p) \end{pmatrix}, \quad (4.6)$$

where the symbol p represents the momentum four-vector with fourth component $p_0 = \omega_p = \pi\nu/\tau$.

It is quite useful to go on from here and define the whole set of matrix n -particle Green's functions which are the expectation values of direct products of n Ψ and Ψ^\dagger operators, time ordered in the usual way. In matrix terms these Green's functions are the direct product of n two-by-two matrices. To derive the equations of motion for these Green's functions we notice that the equal-time anticommutator of $\Psi(1)$ and $\Psi^\dagger(1')$ is the unit matrix times $\delta(\mathbf{r}_1 - \mathbf{r}_1')$. If we introduce the set of spin matrices,

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (4.7)$$

we find that the equation of motion of the spinor Ψ is

$$\begin{aligned} \mathcal{G}_0^{-1}(1)\Psi(1) &= -\text{tr}^{(2)} \int d2 \\ &\times \Psi(2)\Psi^\dagger(2)\tau_3^{(2)}v(1-2)\tau_3^{(1)}\Psi(1), \end{aligned} \quad (4.8)$$

$$\mathcal{G}_0^{-1}(p) \equiv p_0 - \tau_3 \epsilon(p),$$

where the trace is to be taken over the spin indices of the spinors labeled 2. The superscripts 1 and 2 on the spin

matrices indicate the spaces in which these matrices operate. By using the equal-time commutation relations and the equation of motion of the creation spinor, we find that the n -particle spinor Green's function obeys the equation of motion

$$\begin{aligned} \mathcal{G}_0^{-1}(1)\mathcal{G}_n(1\cdots n; 1'\cdots n') \\ = \delta(1-1')\mathcal{G}_{n-1}(2\cdots n; 2'\cdots n') \\ - \delta(1-2')\mathcal{G}_{n-1}(2\cdots n; 1'\cdots n') + \cdots \\ - i \operatorname{tr}^{(n+1)} \int d(n+1) \tau_3^{(1)} v(1-(n+1)) \\ \times \tau_3^{(n+1)} \mathcal{G}_{n+1}(1\cdots n+1; 1'\cdots n+1), \end{aligned} \quad (4.9)$$

where the delta function also includes a delta symbol in the relevant spinor indices.

Nambu has pointed out that the standard Hartree-Fock approximation with the spinor Green's functions yields the BCS solution. When the Hartree-Fock approximation

$$\mathcal{G}_2(12; 1'2') = \mathcal{G}(1-1')\mathcal{G}(2-2') - \mathcal{G}(1-2')\mathcal{G}(2-1') \quad (4.10)$$

is substituted into the one-particle Green's function equation of motion

$$\mathcal{G}_0^{-1}(1)\mathcal{G}_1(1-1') = \delta(1-1') + iV \operatorname{tr}^{(2)} \tau_3^{(1)} \tau_3^{(2)} \mathcal{G}_2(12; 1'2')|_{2=1}, \quad (4.11)$$

the resulting matrix equation takes the form

$$\begin{aligned} \mathcal{G}_0^{-1}(1)\mathcal{G}_1(1-1') = \delta(1-1') \\ + iV \tau_3^{(1)} [\operatorname{tr}^{(2)} \mathcal{G}(0) \tau_3^{(2)}] \mathcal{G}(1-1') \\ - iV \tau_3^{(1)} \mathcal{G}(0) \tau_3^{(1)} \mathcal{G}(1-1'). \end{aligned} \quad (4.12)$$

Since the upper left-hand corner of this equation may be written as

$$\tilde{G}^{-1}(1)G(1-1') = \delta(1-1') + iVF(0)F(1-1'),$$

while the lower left-hand corner is

$$\tilde{G}^{-1}(1)F(1-1') = -iVF(0)G(1'-1),$$

Eqs. (4.10) and (4.12) are identical with (2.32), (2.33), and (2.35).

From this point of view, it is not difficult to derive gauge-invariant Green's function equations of motion. We begin by writing the equation of motion of the two-particle correlation function as

$$\begin{aligned} \mathcal{G}_0^{-1}(1)\mathcal{L}(12; 1'2') = -\delta(1-2')\mathcal{G}(2-1') \\ - i\tau_3^{(1)} V \operatorname{tr}^{(3)} [\tau^{(3)} \mathcal{G}_3(123; 1'2'3)]|_{3=1} \\ - \mathcal{G}(2-2')\mathcal{G}_2(13; 1'3)|_{3=1}, \end{aligned} \quad (4.13)$$

where, as before, the function \mathcal{L} is

$$\mathcal{L}(12; 1'2') = \mathcal{G}_2(12; 1'2') - \mathcal{G}(1-1')\mathcal{G}(2-2'). \quad (4.14)$$

We consider first the limit in which the points 2 and 2'

are far removed from the points 1 and 1'. In this limit, which is appropriate for even moderately long-wavelength and low-frequency electromagnetic disturbances, the important terms in the canonical expansion of the matrix three-particle Green's function are those which contain two-particle correlation functions in which the 2 and 2' indices are not separated. Thus, we include in the expansion of the function G_3 in (4.1) the terms

$$\begin{aligned} \mathcal{G}_3(123; 1'2'3) \cong \mathcal{G}(3-3)\mathcal{L}(12; 1'2') \\ + \mathcal{G}(2-2')\mathcal{G}_2(13; 1'3) - \mathcal{G}(1-3)\mathcal{L}(32; 1'2') \\ - \mathcal{G}(3-1')\mathcal{L}(12; 32') + \mathcal{G}(1-1')\mathcal{L}(23; 2'3), \end{aligned} \quad (4.15)$$

so that the two-particle correlation function satisfies the equation

$$\begin{aligned} \mathcal{G}_0^{-1}(1)\mathcal{L}(12; 1'2') = -\delta(1-2')\mathcal{G}(2-1') \\ + iV \tau_3^{(1)} \mathcal{L}(12; 1'2') \operatorname{tr}^{(3)} \tau_3^{(3)} \mathcal{G}(0) \\ - iV \tau_3^{(1)} \mathcal{G}(0) \tau_3^{(1)} \mathcal{L}(12; 1'2') \\ - iV \tau_3^{(1)} \mathcal{L}(12; 12') \tau_3^{(1)} \mathcal{G}(1-1') \\ + iV \tau_3^{(1)} \mathcal{G}(1-1') \operatorname{tr}^{(3)} \tau_3^{(3)} \mathcal{L}(23; 2'3)|_{3=1}. \end{aligned} \quad (4.16)$$

Equation (4.16) may be used to derive the various forms of the gauge-invariant correlation-function equations which have been discussed in the literature. However, before obtaining the various different forms of these equations, we investigate the properties of the matrix form (4.16).

Let us first note that (4.16) satisfies criterion (a) for gauge invariance since approximation (4.15) is symmetric. In order to verify that criterion (b) is satisfied, we move the second and third terms from the right-hand side of (4.16) to the left and observe that the left-hand side of the rearranged equation is $\mathcal{G}_1^{-1}(1)\mathcal{L}(12; 1'2')$. We then integrate Eq. (4.16), obtaining

$$\begin{aligned} \mathcal{L}(12; 1'2') \\ = -\mathcal{G}(1-2')\mathcal{G}(2-1') \\ - i \int V \mathcal{G}(1-1)\tau_3^{(1)} \mathcal{L}(\bar{1}\bar{2}; \bar{1}\bar{2}')\tau_3^{(1)} \mathcal{G}(\bar{1}-1') \\ + i \int V \mathcal{G}(1-\bar{1})\tau_3^{(1)} \mathcal{G}(\bar{1}-1') \\ \times \operatorname{tr}^{(3)} \tau_3^{(3)} \mathcal{L}(23; 2'3)|_{3=\bar{1}}, \end{aligned} \quad (4.17)$$

which manifests the symmetry of the approximate two-particle correlation function \mathcal{L} .

We finally turn to the solution of Eq. (4.17) which yields gauge-invariant forms for the density and spin density correlation function. We note that the trace of Eq. (4.17) in the matrix space of the spinors 2 and 2' with $2=2'$ yields an expression for the spin density, since

$$\begin{aligned} \operatorname{tr}^{(2)} \Psi(2)\Psi^\dagger(2) = \psi(2+) \psi^\dagger(2+) + \psi^\dagger(2-)\psi(2-) \\ = \text{constant} + \rho(2-) - \rho(2+). \end{aligned} \quad (4.18)$$

On the other hand, if we multiply (4.17) by $\tau_3^{(2)}$ and

then take its trace, we obtain the ordinary particle density when 2 is set equal to 2'. Let us introduce the notation

$$\mathcal{L}^\pm(1-2) = \text{tr}^{(2)}[\tau_3^{(2)}]^\pm \mathcal{L}(12; 12) \quad (4.19)$$

for the correlation function between the matrix $\Psi(1)\Psi^\dagger(1)$ and the particle (spin) density. By setting 1 equal to 1' in (4.17) we obtain

$$\mathcal{L}^+(1-2) = -\mathcal{G}(1-2)\tau_3\mathcal{G}(2-1)$$

$$\begin{aligned} & -i \int V \mathcal{G}(1-\bar{1})\tau_3\mathcal{L}^+(\bar{1}-2)\tau_3\mathcal{G}(\bar{1}-1) \\ & + i \int V \mathcal{G}(1-\bar{1})\tau_3\mathcal{G}(\bar{1}-1)\text{tr}\tau_3\mathcal{L}^+(\bar{1}-2), \end{aligned} \quad (4.20)$$

and

$$\mathcal{L}^-(1-2) = -\mathcal{G}(1-2)\mathcal{G}(2-1)$$

$$-i \int V \mathcal{G}(1-\bar{1})\tau_3\mathcal{L}^-(\bar{1}-2)\tau_3\mathcal{G}(\bar{1}-1), \quad (4.21)$$

where we now have matrix equations in a two-by-two space. In writing Eq. (4.21), we have taken into account the fact that $\text{tr}\mathcal{L}^+(\bar{1}-2)$, the correlation between the ordinary density and the spin density, vanishes identically.

To make further progress with Eqs. (4.20) and (4.21), we employ some matrix properties of the BCS one-particle Green's function. In particular, from Eqs. (4.6) and (2.38) we deduce

$$\Delta\mathcal{G}(p) = -[p_0 + \tau_3\epsilon(p) - \Delta\tau_1]F(p). \quad (4.22)$$

Using this expression in conjunction with the Fourier transform of (4.20) and (4.21), we obtain

$$\begin{aligned} \mathcal{L}^+(q) = & - \int \frac{dp}{(2\pi)^4} \mathcal{G}(p_+)\tau_3\mathcal{G}(p_-)\{1 - iV \text{tr}[\tau_3\mathcal{L}^+(q)]\} \\ & - iV \int \frac{dp}{(2\pi)^4} \mathcal{G}(p_+)\tau_3\mathcal{L}^+(q)\tau_3\mathcal{G}(p_-), \end{aligned} \quad (4.20')$$

$$\begin{aligned} \mathcal{L}^-(q) = & - \int \frac{dp}{(2\pi)^4} \mathcal{G}(p_+)\mathcal{G}(p_-) \\ & - iV \int \frac{dp}{(2\pi)^4} \mathcal{G}(p_+)\tau_3\mathcal{L}^-(q)\tau_3\mathcal{G}(p_-), \end{aligned} \quad (4.21')$$

where $p_\pm = p \pm \frac{1}{2}q$.

With the aid of the identity $\tau_2\mathcal{G}(p)\tau_2 = -\mathcal{G}(-p)$, which may be derived from (4.22), we find on multiplying Eqs. (4.20') and (4.21') by τ_2 on the left and the right and changing the sign of the momentum integrations, that

$$\tau_2\mathcal{L}^\pm(q)\tau_2 = \mp\mathcal{L}^\pm(-q). \quad (4.23)$$

By taking the transpose of Eqs. (4.20') and (4.21') we conclude

$$[\mathcal{L}^\pm(q)]^T = \mathcal{L}^\pm(-q), \quad (4.24)$$

so that

$$\tau_2\mathcal{L}^\pm(q)\tau_2 = \mp[\mathcal{L}^\pm(q)]^T. \quad (4.25)$$

We obtain another identity by multiplying Eqs. (4.20') and (4.21') by τ_1 on the left and on the right and using the relation $\tau_1\mathcal{G}(p)\tau_1 = \mathcal{G}(-\epsilon(p), p_0)$. Since the momentum integral in these equations involves a symmetrical integration over the energy ϵ and the angle z where $\epsilon(p_\pm) \cong \epsilon \pm \frac{1}{2}|q|v_F z$, we may change the sign of the ϵ and the z variables of integration and bring the resulting equations back into their original form. We therefore find that

$$\tau_1\mathcal{L}^\pm(q)\tau_1 = \mp\mathcal{L}^\pm(q). \quad (4.26)$$

It follows from (4.25) and (4.26) that $\mathcal{L}^+(q)$ is given by

$$\mathcal{L}^+(q) = A\tau_3 + B\tau_2, \quad (4.27)$$

while $\mathcal{L}^-(q)$ is given by

$$\mathcal{L}^-(q) = C + D\tau_1. \quad (4.28)$$

Finally, we eliminate the term proportional to τ_1 in \mathcal{L}^- by using the identity $\tau_3\mathcal{L}^-(q)\tau_3 = \mathcal{L}^-(q)$. This identity is derived by multiplying Eq. (4.21') by τ_3 on the left and the right and again changing the sign of the ϵ and z variables of integration.

It is now possible to obtain a trivial solution to Eq. (4.21). Inasmuch as the matrix $\mathcal{L}^-(q)$ must equal $L^{++}(q) - L^{+-}(q)$ times the unit matrix, we obtain from (4.21')

$$\begin{aligned} & [L^{++}(q) - L^{+-}(q)]\{1 + iV[L^{++}(q) - L^{+-}(q)]\}^{-1} \\ & = - \int \frac{dp}{(2\pi)^4} [G(p_+)G(p_-) + F(p_+)F(p_-)]. \end{aligned} \quad (4.29)$$

Except for the denominator on the left-hand side of (4.29), which is approximately unity apart from a minute temperature region near T^c , Eq. (4.29) is identical to the spin correlation function predicted in the BCS approximation. Very near T^c , the denominator on the left of (4.29) predicts a spin analog of zero sound.²¹

Equation (4.20') is only slightly more difficult to solve. Using (4.27), we express $\mathcal{L}^+(q)$ in the form

$$\mathcal{L}^+(q) = [L^{++}(q) + L^{+-}(q)]\tau_3 + 2E(q)\tau_2, \quad (4.30)$$

where $L^{++}(q) + L^{+-}(q)$ is the ordinary density correlation function and $E(q)$, the quantity mentioned earlier, describes the change in the gap energy produced by a density fluctuation. By taking traces to project the parts of Eq. (4.20') proportional to τ_3 and τ_2 we derive the

²¹ L. D. Landau, J. Exptl. Theoret. Phys. **30**, 1058 (1956); **32**, 59 (1957); **35**, 97 (1958) [translation: Soviet Phys.-JETP **30**, 920 (1956); **32**, 101 (1957); **35**, 70 (1958)].

two statements

$$\begin{aligned}
 L^{++}(q) + L^{+-}(q) &= -\frac{1}{2} \int \frac{dp}{(2\pi)^4} \text{tr}[\tau_3 \mathcal{G}(p_+) \tau_3 \mathcal{G}(p_-)] \\
 &\quad \times \{1 - iV[L^{++}(q) + L^{+-}(q)]\} \\
 &\quad + iV \int \frac{dp}{(2\pi)^4} \text{tr}[\tau_3 \mathcal{G}(p_+) \tau_2 \mathcal{G}(p_-)] 2E(q),
 \end{aligned} \quad (4.31)$$

and

$$\begin{aligned}
 2E(q) &= -\frac{1}{2} \int \frac{dp}{(2\pi)^4} \text{tr}[\tau_2 \mathcal{G}(p_+) \tau_3 \mathcal{G}(p_-)] \\
 &\quad \times \{1 - iV[L^{++}(q) - L^{+-}(q)]\} \\
 &\quad + iV \int \frac{dp}{(2\pi)^4} [\tau_2 \mathcal{G}(p_+) \tau_2 \mathcal{G}(p_-)] 2E(q).
 \end{aligned} \quad (4.32)$$

Eliminating $E(q)$, we obtain

$$\begin{aligned}
 [L^{++}(q) + L^{+-}(q)] \{1 - iV[L^{++}(q) + L^{+-}(q)]\}^{-1} \\
 = -T_{33} - iVT_{32}T_{23}[1 - iVT_{22}]^{-1},
 \end{aligned} \quad (4.33)$$

where

$$T_{ij} = \int \frac{dp}{(2\pi)^4} \text{tr} \tau_i \mathcal{G}(p_+) \tau_j \mathcal{G}(p_-). \quad (4.34)$$

The denominator on the left-hand side of (4.33) would be responsible for zero sound if there were a repulsive interaction. Below T_c , this denominator is small and can for most purposes be neglected. If we had included the Coulomb interaction in the Hamiltonian, the same calculational procedure would lead to a term in this denominator of the form $2iv_e(q)[L^{++}(q) + L^{+-}(q)]$. This extra term would give rise to plasma oscillations.

Let us evaluate the traces which appear in (4.33). The first trace which appears is

$$T_{33} = \int \frac{dp}{(2\pi)^4} [G(p_+)G(p_-) - F(p_+)F(p_-)], \quad (4.35)$$

which is the BCS-type result for the two-particle correlation function. The two traces which appear in the numerator of (4.33) are

$$T_{23} = - \int \frac{dp}{(2\pi)^4} F(p_+)F(p_-) \frac{iq_0}{\Delta} = -T_{32}. \quad (4.36)$$

Thus, if the denominator in the second term of (4.33) were close to unity the second term would be quite small and we would recover the BCS correlation function. However, we shall see that this denominator is not close to unity.

By using Eq. (4.22) we can express the denominator

D as

$$\begin{aligned}
 D = 1 + iV \int \frac{dp}{(2\pi)^4} [-p_{0+}p_{0-} + \epsilon(\mathbf{p}_+)\epsilon(\mathbf{p}_-) + \Delta^2] \\
 \times \frac{F(p_+)F(p_-)}{\Delta^2},
 \end{aligned} \quad (4.37)$$

with the restrictions $|\epsilon(\mathbf{p}_+)| < \omega_D$, $|\epsilon(\mathbf{p}_-)| < \omega_D$ on the momentum integration. With the aid of Eq. (2.33), unity may be replaced by integrals of F over the domains $|\epsilon(\mathbf{p}_+)| < \omega_D$ and $|\epsilon(\mathbf{p}_-)| < \omega_D$:

$$1 = -\frac{iV}{2\Delta} \int \frac{dp_+}{(2\pi)^4} F(p_+) - \frac{iV}{2\Delta} \int \frac{dp_-}{(2\pi)^4} F(p_-).$$

Substituting into (4.37) and neglecting terms of order $(|q|v_F/\Delta)^2$ we obtain for D

$$\begin{aligned}
 D \cong iV \int \frac{dp}{(2\pi)^4} \frac{F(p_+)F(p_-)}{2\Delta^2} \{[p_{0+}^2 - \epsilon(\mathbf{p}_-)^2 - \Delta^2] \\
 + [p_{0+}^2 - \epsilon(\mathbf{p}_+)^2 - \Delta^2] - 2p_{0+}p_{0-} + 2\epsilon(\mathbf{p}_+)\epsilon(\mathbf{p}_-) + 2\Delta^2\},
 \end{aligned}$$

which simplifies to

$$D \cong \frac{iV}{2\Delta^2} \int \frac{dp}{(2\pi)^4} F(p_+)F(p_-) [q_0^2 - (|q|v_F z)^2]. \quad (4.38)$$

Hence, the denominator in question is only of order V , and vanishes in the low-frequency and low-wave-number limit. The correction term to the BCS theory, the second term in Eq. (4.33), may therefore be quite large.

By substituting the results of our trace evaluations into (4.33), we find that

$$\begin{aligned}
 [L^{++} + L^{+-}] \{1 - iV[L^{++} + L^{+-}]\}^{-1} \\
 = - \int \frac{dp}{(2\pi)^4} [G(p_+)G(p_-) - F(p_+)F(p_-)a(q)],
 \end{aligned} \quad (4.39)$$

where

$$\begin{aligned}
 a(q) &= \frac{q_0^2 A_0(q) + q^2 v_F^2 A_2(q)}{q_0^2 A_0(q) - q^2 v_F^2 A_2(q)}, \\
 A_0(q) &= \int \frac{dp}{(2\pi)^4} F(p_+)F(p_-), \\
 A_2(q) &= \int \frac{dp}{(2\pi)^4} z^2 F(p_+)F(p_-).
 \end{aligned} \quad (4.40)$$

In evaluating these expressions it is necessary to recall their symbolic nature. We must keep in mind, for example, that Eq. (4.39) does not describe the Fourier transform of the density correlation function, but the Fourier coefficients of a Fourier series representation over a restricted time domain. That is to say, the fourth

component of q , q_0 , takes on the values $q_{0\nu} = i\pi\nu/\beta$ where ν is an even integer. Moreover, the integrals in (4.39) and (4.40) consist of momentum integrations and summation over all values of p_0 together with multiplication by $(i\beta)^{-1}$. The values of $p_{0\pm}$ are $p_{0\nu\pm} = i\pi\nu_{\pm}/\beta$, where ν_{\pm} are odd integers. Thus the right-hand side of (4.39), $Y(\mathbf{q}, q_{0\nu})$, is explicitly equal to

$$Y = \int \frac{dp}{(2\pi)^3} \left(\frac{i}{\beta} \right) \sum_{\nu} \left[\frac{p_{0\nu+} + \epsilon(\mathbf{p}_+)}{p_{0\nu+}^2 - E^2(\mathbf{p}_+)} \right. \\ \times \frac{(p_{0\nu+} - q_{0\nu}) + \epsilon(\mathbf{p}_-)}{(p_{0\nu+} - q_{0\nu})^2 - E^2(\mathbf{p}_-)} a(q) \frac{\Delta}{p_{0\nu+}^2 - E^2(\mathbf{p}_+)} \\ \left. \times \frac{\Delta}{(p_{0\nu+} - q_{0\nu})^2 - E^2(\mathbf{p}_-)} \right]. \quad (4.39')$$

To perform the summation over $p_{0\nu+}$ we expand the denominator into partial fractions. Using the even character of Y with respect to $q_{0\nu}$, and its invariance under interchange of \mathbf{p}_+ and \mathbf{p}_- , we obtain for $Y(\mathbf{q}, q_{0\nu})$

$$Y = i \int \frac{dp}{(2\pi)^3} \frac{E_+(E_+ - q_{0\nu}) + \epsilon_+ \epsilon_- + \Delta^2 a(q)}{2E_+ E_-} \tanh \frac{1}{2} \beta E_+ \\ \times \{ 1/(E_+ - E_- - q_{0\nu}) - 1/(E_+ + E_- - q_{0\nu}) \\ + (q_{0\nu} \leftrightarrow -q_{0\nu}) \} \quad (4.41) \\ = i \rho_E \int_{-1}^{+1} \frac{dz}{2} \int \frac{d\epsilon}{2} A(q, \epsilon) \\ \times [E_+(E_+ - q_{0\nu}) + \epsilon_+ \epsilon_- + \Delta^2 a(q)], \quad (4.42)$$

where $\epsilon_{\pm} = \epsilon(\mathbf{p}_{\pm})$, $E_{\pm} = E(\mathbf{p}_{\pm})$, and

$$A(q, \epsilon) = \frac{\tanh \frac{1}{2} \beta E_+}{E_+} \\ \times \left[\frac{1}{(E_+ - q_{0\nu})^2 - E_-^2} + \frac{1}{(E_+ + q_{0\nu})^2 - E_-^2} \right]. \quad (4.43)$$

The function $A(q, \epsilon)$ just defined is also needed for the evaluation of $a(q)$ since Eq. (4.40) may be written in the form

$$A_n(q) = \int_{-1}^{+1} \frac{dz}{2} \int \frac{d\epsilon}{2} A(q, \epsilon). \quad (4.44)$$

To determine the retarded commutator of the densities we proceed as in Sec. 2. We let q_0 in (4.39) be a complex variable in such a way that the ensuing function is analytic at infinity. Then for times $-i\beta > t > t'$ we multiply by $[1 - e^{-q_0\beta}]^{-1} e^{-i q_0(t-t')}$. An integral along any contour passing between the singularities of this factor and the integrand of the symbolic integral (4.39) yields the Fourier representation of the time-ordered

product for $t > t'$. The imaginary part of this integral represents one-half the commutator for $t > t'$. Since the Fourier transform is real when q_0 is real, the imaginary part of the integral involves the odd part of the Fourier transform. Moreover, since the Fourier coefficient is an even function of the real part of q_0 and an odd function of its imaginary part, the commutator for $t > t'$ is the contour integral surrounding the real axis of the Fourier coefficient treated as a function of complex q_0 and multiplied by $e^{-i q_0(t-t')}$. The Fourier transform of the retarded commutator is therefore the limit of the Fourier coefficient treated as a function of a complex variable q_0 , as q_0 approaches the real axis from below. Correspondingly, the transform of the advanced commutator is the limit of the Fourier coefficient function as q_0 approaches the real axis from above. Thus the symbolic equation (4.39) is an explicit equation for the Fourier transform of the retarded commutator. Using the relation between this commutator and the electromagnetic properties [Eqs. (3.20), (3.23), and (3.27)] we conclude that

$$\frac{-i q^2 [\alpha^L + (\sigma^L / i q_0) \epsilon(\text{Im} q_0)]}{e^2 - V q^2 [\alpha^L + (\sigma^L / i q_0) \epsilon(\text{Im} q_0)]} = Y(|\mathbf{q}|, q_0), \quad (4.45)$$

where q_0 is a complex variable with infinitesimal imaginary parts and e the electronic charge.

We have now reduced the determination of the longitudinal polarizability and conductivity to the calculation of certain double integrals. These integrals lead to a considerably more general result than the random phase approximation. In particular, Eq. (3.80) represents an evaluation of the longitudinal response coefficients at finite temperatures. At zero temperature, Anderson and others have found the position of the pole in the denominator of $a(q)$ in the limit of small q . They point out that in the zero-temperature, low-wave-number limit, this pole exhausts the sum rule on the conductivity. On the other hand, the random phase approximation does not provide a method of evaluating the weights of several singularities of a function like L . Thus, the random phase approximation does not adequately describe the finite temperature behavior of the superconductor where an isolated sound-wave pole is replaced by a continuum of singularities of L , even when \mathbf{q} and q_0 are small. To describe this continuum of singularities, we must approximately evaluate the denominator of $a(q)$ in the low-frequency, low-wave-number limit.

We begin by expanding $A(q, \epsilon)$ in the partial fraction from (4.41) to the lowest order in $|\mathbf{q}|$ and q_0

$$A(q, \epsilon) = \frac{\tanh \frac{1}{2} \beta E_+}{2E^2} \left[-\frac{1}{E} + \frac{2(\epsilon |\mathbf{q}| v_F z / E)}{(\epsilon |\mathbf{q}| v_F z / E)^2 - q_0^2} \right]. \quad (4.46)$$

Only the portion of this expression even in z contributes to $A_0(q)$ and $A_2(q)$ and consequently in determining

$a(q)$ we may replace $A(q, \epsilon)$ by $A^{(v)}(q, \epsilon)$, where

$$A^{(v)}(q, \epsilon) = \frac{1}{2E^2} \left\{ -\frac{\tanh \frac{1}{2}\beta E}{E} + \frac{\partial}{\partial E} (\tanh \frac{1}{2}\beta E) \frac{(\epsilon q v_F z/E)^2}{(\epsilon q v_F z/E)^2 - q_0^2} \right\}. \quad (4.47)$$

When $\beta \rightarrow \infty$, $A^{(v)}(q, \epsilon)$ approaches $-\frac{1}{2}E^{-3}$ and the quotient $a(q)$ becomes

$$a(q) = [q_0^2 + \frac{1}{3}(\mathbf{q}v_F)^2] / [q_0^2 - \frac{1}{3}(\mathbf{q}v_F)^2]. \quad (4.48)$$

In this limit the function Y approaches $\frac{1}{2}i\rho_B a(q)$ and

$$-\frac{q_0 e^2}{q^2} Y \epsilon(\text{Im} q_0) \rightarrow \frac{\pi n e^2}{m} \delta(q_0^2 - \frac{1}{3}q^2 v_F^2) \frac{|\mathbf{q}| v_F}{\sqrt{3}}. \quad (4.49)$$

Since the product (4.49) is equal to σ^L for small values of q , we conclude that the conductivity sum rule is entirely exhausted by the collective mode at the classically determined sound velocity $v_F/\sqrt{3}$.

At finite temperatures the second term in (4.47) cannot be neglected. It gives rise to a term in the approximate dispersion equation for the sound velocity which results in a complex solution even in the long-wavelength limit. The imaginary part of this velocity is exponentially small at temperatures low compared to the transition temperature, but even at the lowest temperatures it is to be contrasted with the dispersion equation for classical sound. The latter yields a sound velocity whose imaginary part approaches zero at arbitrary temperatures in the long-wavelength limit. We may say physically that the excitations present at finite temperatures provide a mechanism for decay of collective modes with arbitrarily small wavelengths. The damping increases with temperature leaving little vestige of a single frequency for each wave number near the transition temperature.

It is perhaps worth recalling that these conclusions are based on an approximation which neglects the lifetimes necessary for the canonical treatment of sound waves. The latter phenomenon occurs when relaxation to local equilibrium takes place in a time τ short compared to the period of the disturbance. It is absent in a perfect Fermi or Boltzmann gas, as it is near the critical temperature in a superconductor. We might therefore guess that a calculation including these relaxation phenomena would nullify the conclusions derived above and lead to a sharply defined mode for very long wavelengths. If it did so in a one-component system we would expect diffusion to play a significant role in the two-component system of phonons and electrons. Indeed, a crude calculation we have performed appears to lead to a diffusion pole which exhausts the sum rule at $q_0 = -iq^2 v_F^2 \frac{1}{3} \tau_T$, where τ_T is of the order of the phonon emission time.

We conclude this section by reminding the reader that the effect of the long-range Coulomb interaction on α' is determined in this approximation by substituting (4.45) into (3.31). The sound-wave pole in α' at vanishing temperature and the continuum at finite temperatures are replaced by the plasma pole in the familiar fashion and this pole is only negligibly modified by the superconducting transition.

5. LIFETIME-DEPENDENT PROPERTIES

To understand the quasi-thermodynamic properties of a system, such as electrical conductivity, thermal conductivity, and the propagation of sound waves, it is necessary to account for the restoration of local equilibrium during sufficiently slowly varying disturbances. Consequently, as we indicated in Secs. 3 and 4, more exact correlation functions than those heretofore employed are required for the discussion of low-frequency and low-wave-number dissipative responses. In particular, we must utilize single-particle correlation functions which are accurate enough to exhibit the decay of states formed by adding or subtracting a particle to the system in equilibrium.

In Sec. 5 of I a simple estimate for this width, or inverse decay time, Γ , was derived from terms in an approximate expression for $G_2 - G_1 G_1$ which died away quite rapidly with distance. These terms yielded for Γ an appropriately averaged product of the density of interacting particles, the interaction cross section, and the relative velocity [cf. I, Eq. (5.102)]. The terms responsible for this width were eliminated by the approximation for G_2 , (2.8), which led to the solutions (2.28) and (2.30), but they could clearly be included in a better approximation to G_2 . We have estimated these widths for our simple Hamiltonian by retaining the previously eliminated terms. Above the critical temperature, as at all temperatures in normal substances, these widths lead to the replacement of the spectral function $\bar{A}(\epsilon, \omega) = 2\pi\delta(\omega - \epsilon)$ of a Hartree approximation by a spectral function of the form

$$A(\epsilon, \omega) = \frac{\Gamma(\epsilon, \omega)}{(\omega - \epsilon)^2 + [\frac{1}{2}\Gamma(\epsilon, \omega)]^2}. \quad (5.1)$$

Below the critical temperature, they introduce a spread in both parts, $\delta(\omega - E)$ and $\delta(\omega + E)$, of the function $\delta(\omega^2 - E^2)$ which appears in the superconducting spectral representation, (2.34).

By taking these lifetimes into account we can immediately derive a quantum-mechanical approximation for the conductivity similar to the well-known collision-time treatment. Like this familiar simplified description, the first quantum-mechanical approximation neglects the interrelations between scatterings which guarantee momentum and energy conservation, and therefore it does not result in a full Boltzmann-like equation for $G_2 - G_1 G_1$. The omission of these effects has the well-

known defect that the two-particle cross section occurring in the approximate conductivity is the scattering cross section rather than a transport cross section in which forward scatterings are ineffective.²² In our crude model of the superconductor, there is little point in considering more refined corrections of this character.

In fact, there is little point in employing the widths deduced from the simple model, since they have so little to do with reality. The calculation of the width is quite sensitive to the form of the interaction and quite different for our simple interaction and the actual time-dependent electron-phonon interaction. The interactions involving particles within a small range of the Fermi surface and described by the model Hamiltonian give rise to a lifetime considerably longer than we would expect from a realistic interaction which describes phonon emission, and also longer than that deduced experimentally from various lifetime-dependent effects.

$$\omega\sigma(k^2\omega^2) = \frac{ne^2}{m} \tanh\frac{1}{2}\beta\omega \int_{-1}^{+1} \frac{dz}{2} (1-z^2) \int_{-\omega_D}^{\omega_D} d\epsilon \int \frac{d\omega'}{2\pi} \text{Re} \frac{[\omega_+ - \epsilon_+ - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega_+][\omega_- - \epsilon_- - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega_-]}{[(\omega_+ - \epsilon_+)^2 + (\frac{1}{2}\Gamma)^2][(\omega_- - \epsilon_-)^2 + (\frac{1}{2}\Gamma)^2]}. \quad (5.3)$$

The real part of this integral may be rewritten in the form

$$\omega\sigma^T(k^2\omega^2) = \frac{ne^2}{m} \int \frac{dz}{2} \int d\epsilon \int \frac{d\omega'}{2\pi} \frac{\frac{3}{2}\Gamma(1-z^2)}{\Gamma^2 + (\omega - kv_F z)^2} \times \frac{(\frac{1}{2}\Gamma)^2 [\tanh\frac{1}{2}\beta\omega_+ - \tanh\frac{1}{2}\beta\omega_-]}{[(\omega_+ - \epsilon_+)^2 + (\frac{1}{2}\Gamma)^2][(\omega_- - \epsilon_-)^2 + (\frac{1}{2}\Gamma)^2]}. \quad (5.4)$$

Performing two integrations, we derive

$$\sigma^T(k^2\omega^2) = \frac{ne^2}{m} \int_{-1}^{+1} \frac{dz}{2} \frac{\frac{3}{2}\Gamma(1-z^2)}{\Gamma^2 + (\omega - kv_F z)^2}, \quad (5.5)$$

so that when Γ approaches zero, σ becomes

$$\sigma^T(k^2\omega^2) = (\pi ne^2/2m) \frac{3}{2} [1 - (\omega/kv_F)^2] \eta(kv_F - |\omega|). \quad (5.6)$$

This limit is approximately correct when kv_F or ω is much larger than Γ , but ill-defined when k and ω approach zero. The lack of a limit reflects the dependence on the boundaries of the dissipation of slowly varying disturbances when there is no mechanism (or lifetime) for restoring equilibrium more rapidly. As long as Γ is not equal to zero, the boundaries are irrelevant and the approximation to σ approaches a well-defined limit as k and ω approach zero. This limit is the familiar expression

$$\lim_{k \rightarrow 0} \lim_{\omega \rightarrow 0} \sigma(k^2\omega^2) = \frac{ne^2}{m} \frac{1}{\Gamma}. \quad (5.7)$$

When we perform the analogous calculation for the

To allow for this deviation we treat the width as an additional experimental parameter.

Our object is to determine thermal and electric conductivities from this parameter and to investigate the effect of superconductive transitions on these conductivities.

To indicate how widths modify our calculations at low wave number and frequency, we first consider a normal metal. The Green's function associated with the weight function (5.1) takes the form

$$G(\epsilon, \omega) \cong \frac{\omega - \epsilon}{(\omega - \epsilon)^2 + (\frac{1}{2}\Gamma)^2} - \frac{1}{2}i \tanh\frac{1}{2}\beta\omega \frac{\Gamma}{(\omega - \epsilon)^2 + (\frac{1}{2}\Gamma)^2} \quad (5.2)$$

on the real axis. In a normal metal, $\Delta=0$, so that the approximation for the conductivity becomes

superconductor, similar results are obtained. The function $\sigma(k^2\omega^2)$ is altered from the form derived in the previous section when kv_F and ω are small compared to Γ . The limit of the approximation to $\sigma(k^2\omega^2)$ as k and ω approach zero is then well defined. Indeed, if $\Gamma \ll \Delta$, the ratio of the quasi-static, quasi-uniform conductivity in a superconductor to that in a normal metal is precisely what we would guess from the two-fluid model: $1 - S_T(0)$.

We sketch this calculation very briefly. The introduction of widths in the superconducting Green's function in a form appropriate to phonon emission and absorption is accomplished by the analog of (5.1) for the Green's function in (2.34):

$$A(\epsilon, \omega) = \frac{\Gamma}{2E} \left[\frac{E + \epsilon}{(\omega + E)^2 + (\frac{1}{2}\Gamma)^2} + \frac{E - \epsilon}{(\omega - E)^2 + (\frac{1}{2}\Gamma)^2} \right], \quad (5.8)$$

$$G(\epsilon, \omega) = \frac{E + \epsilon}{2E} \left[\frac{\omega - E - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega}{(\omega - E)^2 + (\frac{1}{2}\Gamma)^2} \right] + \frac{E - \epsilon}{2E} \left[\frac{\omega + E - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega}{(\omega + E)^2 + (\frac{1}{2}\Gamma)^2} \right], \quad (5.9)$$

$$F(\epsilon, \omega) = -\frac{\Delta}{2E} \left[\frac{\omega - E - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega}{(\omega - E)^2 + (\frac{1}{2}\Gamma)^2} \right] + \frac{\Delta}{2E} \left[\frac{\omega + E - \frac{1}{2}i\Gamma \tanh\frac{1}{2}\beta\omega}{(\omega + E)^2 + (\frac{1}{2}\Gamma)^2} \right]. \quad (5.10)$$

These forms, like (5.1), are of course only qualitatively correct. In the superconductor they are valid, and similar to the correlation functions of the previous section, only when Γ is much less than Δ . As ω and k

²² S. F. Edwards, *Phil. Mag.* **33**, 1020 (1958); A. A. Abrikosov and L. P. Gor'kov, reference 4. The work of W. Kohn and J. Luttinger, *Phys. Rev.* **108**, 590 (1957) is also related.

approach zero, the integral for the conductivity in the analogous approximation simplifies to

$$\left. \begin{aligned} \lim_{\omega \rightarrow 0} \sigma^{++}(0\omega^2) &= \frac{ne^2}{m} \frac{1}{\Gamma} \int_0^\infty d\epsilon \frac{\epsilon^2 + E^2}{2E^2} \frac{\partial}{\partial E} (\tanh \frac{1}{2}\beta E), \\ \lim_{\omega \rightarrow 0} \sigma^{+-}(0\omega^2) &= \frac{ne^2}{m} \frac{1}{\Gamma} \int_0^\infty d\epsilon \frac{\Delta^2}{2E^2} \frac{\partial}{\partial E} (\tanh \frac{1}{2}\beta E), \\ \lim_{\omega \rightarrow 0} \sigma(0\omega^2) &= \frac{ne^2}{m} \frac{1}{\Gamma} S_T(0), \end{aligned} \right\} \quad (5.11)$$

with Γ assumed much smaller than Δ . The expressions for ν^{++} and ν^{+-} at low frequencies are only slightly altered from those in Sec. 4.

In order to discuss thermal conductivity in an analogous fashion, we must identify a heat density and a heat current. One way to make this identification is to examine the behavior of perturbations from the equilibrium values of densities of the conserved variables—matter, energy, and momentum. A somewhat lengthy analysis of the propagation of these disturbances leading to sound- and thermal-conduction equations will be the subject of a separate paper. A result of that discussion is a mathematical formulation of the physically obvious notion that the flow of heat corresponds to the flow of energy with no flow of matter. This leads to the identification of a density operator, h , which takes the form

$$h(\mathbf{r}t) = \epsilon(\mathbf{r}t) - N^{-1}(E + pV)n(\mathbf{r}t), \quad (5.12)$$

where $\epsilon(\mathbf{r}t)$ is the energy density and $n(\mathbf{r}t)$ the particle density. This expression reduces to the familiar $\epsilon - \mu n$ when $TS \rightarrow 0$. Correspondingly the heat current operator \mathbf{j}^h is defined by²³

$$\mathbf{j}^h(\mathbf{r}t) = \mathbf{j}^\epsilon(\mathbf{r}t) - N^{-1}(E + pV)\mathbf{j}^n(\mathbf{r}t) \quad (5.13)$$

in terms of the matter current operator \mathbf{j}^n ,

$$\mathbf{j}^n(\mathbf{r}) = (-i/2m) \sum_s [\psi^\dagger(\mathbf{r}) \nabla \psi(\mathbf{r}) - (\nabla \psi^\dagger(\mathbf{r})) \psi(\mathbf{r})], \quad (5.14)$$

and the energy current operator $\mathbf{j}^\epsilon(\mathbf{r}t)$. The latter is, of course, nonlocal in the same sense as the momentum current operator $\mathbf{T}_{ij}(\mathbf{r}t)$ [cf. I, Eq. (2.33)]. In a system with local two-body forces it takes the form

$$\begin{aligned} \mathbf{j}_k^\epsilon(\mathbf{r}) &= \frac{1}{(2m)^2} \sum_s [(\nabla \psi^\dagger(\mathbf{r})) \nabla_k \nabla \psi(\mathbf{r}) \\ &\quad - (\nabla_k \nabla \psi^\dagger(\mathbf{r})) \nabla \psi(\mathbf{r})] + \frac{1}{4} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \\ &\quad \times \{\mathbf{j}_k^n(\mathbf{r}), \rho(\mathbf{r}')\}. \end{aligned} \quad (5.15)$$

²³ The same expression has been inferred by rather different methods by H. Mori, Phys. Rev. 111, 694 (1958); 112, 829 (1958). See also H. Mori, I. Oppenheim, and J. Ross, Progr. in Stat. Mech. 1, (1960) (to be published). Equivalent but less tractable expressions were previously obtained by M. S. Green, J. Chem. Phys. 22, 398 (1954).

Just as an induced static electrical current obeys

$$\langle \mathbf{j}^L(\mathbf{r}t) \rangle = -2 \int_{-\infty}^t d\mathbf{r}' dt' \times \sigma'^L(\mathbf{r} - \mathbf{r}', t - t') \nabla' \phi(\mathbf{r}'t'), \quad (5.16)$$

where σ'^L is the commutator

$$-2i \nabla \sigma'^L(\mathbf{r} - \mathbf{r}', t - t') = \langle [\mathbf{j}(\mathbf{r}t), \rho(\mathbf{r}'t')] \rangle, \quad (5.17)$$

an induced heat current satisfies

$$\langle \mathbf{j}^h(\mathbf{r}t) \rangle = -2 \int_{-\infty}^t d\mathbf{r}' dt' \times T_K(\mathbf{r} - \mathbf{r}', t - t') \nabla' \delta T(\mathbf{r}'t'), \quad (5.18)$$

where δT is the temperature perturbation and

$$-2i T \nabla K(\mathbf{r} - \mathbf{r}', t - t') = \langle [\mathbf{j}^h(\mathbf{r}t), \rho^h(\mathbf{r}'t')] \rangle. \quad (5.19)$$

This relation leads us to define a frequency- and wave number-dependent thermal conductivity tensor in analogy with the electrical conductivity tensor. In particular, we may write

$$\langle [\mathbf{j}_k^h(\mathbf{r}t), \mathbf{j}_l^h(\mathbf{r}'t')] \rangle = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')} \omega T_{Kkl}(\mathbf{k}\omega). \quad (5.20)$$

Using the relation between the commutator and the anticommutator we may write a fluctuation-dissipation formula for the longitudinal thermal conductivity $\kappa(k^2\omega^2)$ analogous to (I, 4.66) for the electrical conductivity κ

$$\begin{aligned} \frac{1}{2} \langle \{\mathbf{j}_k^h(\mathbf{r}t), \mathbf{j}_l^h(\mathbf{r}'t')\} \rangle \\ = \int \frac{d\mathbf{k}}{(2\pi)^3} \int \frac{d\omega}{2\pi} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\omega(t - t')} \omega T_{Kkl} \\ \times (\mathbf{k}, \omega) \coth \frac{\beta\omega}{2}. \end{aligned} \quad (5.21)$$

In particular, the observed low-frequency and low-wave-number response takes the form

$$\delta_{kl} T_K(00) = \delta_{kl} T_K = \frac{\beta}{4} \int d\mathbf{r} \int dt \langle \{\mathbf{j}_k^h(\mathbf{r}t), \mathbf{j}_l^h(00)\} \rangle. \quad (5.22)$$

Before turning to the superconductor we apply these expressions to a weakly interacting, highly degenerate Fermi gas. Since the entropy of such a gas is negligible, we replace $E + pV$ by μN and \mathbf{j}^h by $\mathbf{j}^\epsilon - \mu \mathbf{j}^n$. To determine \mathbf{j}^h , we introduce the expressions (5.13) and (5.15) for \mathbf{j}^ϵ and \mathbf{j}^n , writing

$$\begin{aligned} \mathbf{j}_k^h(1) &= \sum_s \left[\frac{\nabla_1 \cdot \nabla_1'}{2m} - \mu \right] \frac{(\nabla_1 - \nabla_1')_k}{2mi} \psi^\dagger(1') \psi(1) \Big|_{1'=1} \\ &\quad + \frac{1}{4} \int d\mathbf{r}' \{ \rho(\mathbf{r}), \mathbf{j}_k^n(\mathbf{r}') \} v(\mathbf{r} - \mathbf{r}'). \end{aligned} \quad (5.23)$$

Since the leading term in the thermal conductivity of a weakly interacting gas is proportional to $(1/\Gamma)$ and therefore diverges as the square of the reciprocal potential strength, we may presume that terms in the heat current proportional to the potential will be relatively negligible. We may then replace (5.23) by

$$\mathbf{j}_k^h(1) = \sum_s \left[\frac{\nabla_1 \cdot \nabla_1'}{2m} - \frac{p_F^2}{2m} \right] \frac{(\nabla_1 - \nabla_1')_k}{2mi} \psi(1') \psi(1) \Big|_{1'=1}. \quad (5.24)$$

With this replacement, the heat-current correlation function becomes

$$\begin{aligned} \langle \mathbf{j}_k^h(1) \mathbf{j}_l^h(2) \rangle_+ &= - \sum_{s_1 s_2} \frac{(\nabla_1 - \nabla_1')_k}{2mi} \frac{(\nabla_2 - \nabla_2')_l}{2mi} \left[\frac{\nabla_1 \cdot \nabla_1'}{2m} - \frac{p_F^2}{2m} \right] \\ &\times \left[\frac{\nabla_2 \cdot \nabla_2'}{2m} - \frac{p_F^2}{2m} \right] G_2^{s_1 s_2}(12; 1'2') \Big|_{1'=1^+, 2'=2^+}. \end{aligned} \quad (5.25)$$

To evaluate the expression (5.25) approximately, we write G_2 in terms of products of one-particle Green's functions and note that only the exchange term contributes. Then, by the same analysis which led to (3.38) and (3.39), we obtain for the frequency- and wave number-dependent conductivity

$$\begin{aligned} \omega \kappa(k^2 \omega^2) \coth \frac{1}{2} \beta \omega &= \frac{1}{T} \frac{2}{m^2} \int \frac{d\mathbf{k}'}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \\ &\times \frac{(\mathbf{k}' \cdot \mathbf{k})^2 \left[k'^2 - \frac{1}{4} k^2 - p_F^2 \right]^2}{k^2 \left[\frac{2}{m} \right]} \\ &\times \text{Re}[G(\mathbf{k}_+ \omega_+) G(\mathbf{k}_- \omega_-)]. \end{aligned} \quad (5.26)$$

We determine $\kappa(00) \equiv \kappa$ by repeating the operations we applied in evaluating $\sigma(00)$. Thus, we introduce the variables ϵ , z , and ω' , expressing (5.26) as

$$\kappa T = \frac{\beta}{2} \frac{n}{m} \int d\epsilon \int \frac{d\omega'}{2\pi} \int \frac{dz}{2} \frac{-3z^2 \epsilon^2 \left(\frac{1}{2} \Gamma \right)^2 \text{sech}^2 \left(\frac{1}{2} \beta \omega' \right)}{[(\omega' - \epsilon)^2 + \left(\frac{1}{2} \Gamma \right)^2]}. \quad (5.27)$$

Performing the trivial z integration, and the frequency integration in the limit $\beta \Gamma \ll 1$, we find

$$\kappa T = \frac{\beta}{2} \frac{n}{m} \int \frac{d\epsilon}{2} \frac{\epsilon^2}{\Gamma} \text{sech}^2(\beta \epsilon / 2), \quad (5.28)$$

which reduces to

$$\kappa = \frac{1}{3} \pi^2 (n/m) (k_B^2 T / \Gamma), \quad (5.29)$$

where we have explicitly introduced Boltzmann's constant $k_B = (\beta T)^{-1}$. Comparing this result with the expression derived for the electrical conductivity, we obtain the Wiedemann-Franz law:

$$\kappa / \sigma T = \frac{1}{3} \pi^2 (k_B^2 / e^2), \quad (5.30)$$

for the ratio of thermal and electrical conductivities.

The Wiedemann-Franz law serves to indicate both the strengths and weaknesses of our calculational procedures. Metals do obey this law over a wide range of conditions, but they do not obey it very well at low temperatures. The source of its failure is well understood. As we indicated at an earlier stage, restrictions connected with persistence of velocity lead to the replacement of the cross section in the width which characterizes the electrical conductivity by a transport cross section $\int \sigma(\theta) (1 - \cos \theta) d\Omega$. This replacement is not very significant when the scattering is due to impurities, but it is extremely important when the scattering is due to phonons and $\theta \approx (k_B T) / \omega_D$. The corresponding corrections to the thermal conductivity are considerably less important, since almost-forward scattering contributes to the thermal resistivity.

We may corroborate our assertion about the relative importance of interrelationships among the scatterings for thermal and electrical conductivity by observing that the derived temperature dependence of the electronic thermal conductivity is correct when this conductivity is limited by lattice scattering, although the derived temperature dependence of the electrical conductivity is not. When phonon scattering predominates, the number of scatterers and therefore the width Γ is proportional to T^3 . The predicted thermal conductivity is therefore proportional to T^{-2} , in agreement with experiment and more careful calculation. The predicted electrical conductivity is correspondingly proportional to T^{-3} . When we take into account the correction due to the ineffectiveness of the dominant forward scattering, $(1 - \cos \theta \approx \theta^2 \approx T^2)$, we deduce the temperature dependence derived from more accurate calculations and also from experiment, namely, $\sigma \approx T^{-5}$. An estimate of the absolute electrical conductivity from our approximate G_2 is therefore less trustworthy than a calculation of the thermal conductivity from it. Since the corrections to σ are likely to be similar in normal and superconducting phases, the evaluated ratio of electrical conductivities in the two phases is probably more accurate than the estimate for either phase.

Although our estimate of the thermal conductivity as limited by lattice scattering is essentially correct for normal metals, we cannot, of course, guarantee that the collision time is not strongly altered by the occurrence of the gap. Indeed this is the essential difference between the phenomenological approach we take and that of

BRT.²⁴ We shall see that this assumption appears to agree with experiments on several elements for which $\beta\Gamma \ll 1$. The same assumption, of a mean free time relatively independent of the excitation, is not appropriate for impurity scattering. This kind of scattering gives rise to widths which depend on momentum in a manner best described by a relatively constant mean free path. The results we now derive therefore, at best, apply only to the very purest superconductors; the additional thermal resistance caused by impurity scattering will be considered presently.

In a superconductor, the term in heat current that involves the potential strength cannot be immediately discarded. Indeed, we might expect large contributions to arise from the second term in

$$\mathbf{j}^h(1) = \left[\frac{\nabla_1 \cdot \nabla_1'}{2m} - \frac{p_F^2}{2m} \right] \frac{(\nabla_1 - \nabla_1')_k}{2mi} \sum_s \psi^\dagger(1') \psi(1) \Big|_{1'=1} + \frac{1}{4} V \{n(1) - \langle n(1) \rangle, \mathbf{j}^n(1)\}. \quad (5.31)$$

A more careful analysis indicates that such suspicions are unfounded and that the effect of the second term is quite small. Consequently, we only consider the first term in (5.31) and once more express the heat-current correlation function in the form (5.25). As in the evaluation of the electrical conductivity, we introduce the Green's functions for the superconductor. Corresponding to (5.26) we have

$$\omega T\kappa(k^2\omega^2) \coth \frac{1}{2}\beta\omega$$

$$= \frac{2}{m^2} \int \frac{dk'}{(2\pi)^3} \int \frac{d\omega'}{2\pi} \frac{(\mathbf{k}' \cdot \mathbf{k})^2}{k^2} \left[\frac{k'^2 - \frac{1}{4}k^2 - p_F^2}{2m} \right]^2$$

$$\times \text{Re}[G(\mathbf{k}_+, \omega_+) G(\mathbf{k}_-, \omega_-) + F(k_+, \omega_+) F(k_-, \omega_-)], \quad (5.32)$$

with F and G given by (5.9) and (5.10). Introducing the variables ϵ , ω , and z , and performing the z integration, we obtain

$$\delta_{kl} T\kappa = \beta \int dt_1 \int d\mathbf{r}_1 \exp\left(-\frac{r_1}{l}\right) \left[\frac{\nabla_1 \cdot \nabla_1'}{2m} - \frac{p_F^2}{2m} \right] \left[\frac{\nabla_2 \cdot \nabla_2'}{2m} - \frac{p_F^2}{2m} \right]$$

$$\times \frac{(\nabla_1 - \nabla_1')_k (\nabla_2 - \nabla_2')_l}{2mi \cdot 2mi} \text{Re}[G(1-2') G(2-1') + F(1-2) F(2'-1')] \Big|_{2'=2=0, 1'=1}, \quad (5.36)$$

where the functions F and G still include the effect of phonon absorption. To evaluate the thermal conductivity from (5.40), we again insert Fourier transforms, writing

²⁴ J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959), referred to as BRT.

$$T\kappa = \frac{\beta}{2} \frac{n}{m} \int d\epsilon \int \frac{d\omega'}{2\pi} \frac{\epsilon^2}{4E^2} \left(\frac{1}{2}\Gamma \right)^2 \text{sech}^2\left(\frac{1}{2}\beta\omega'\right)$$

$$\times \left\{ \left[\frac{E+\epsilon}{(\omega'-E)^2 + (\frac{1}{2}\Gamma)^2} + \frac{E-\epsilon}{(\omega'+E)^2 + (\frac{1}{2}\Gamma)^2} \right]^2 \right.$$

$$\left. + \left[\frac{\Delta}{(\omega'-E)^2 + (\frac{1}{2}\Gamma)^2} - \frac{\Delta}{(\omega'+E)^2 + (\frac{1}{2}\Gamma)^2} \right]^2 \right\} \quad (5.33)$$

When Γ is much smaller than both Δ and β^{-1} , the frequency integration can be carried out directly, with the result

$$T\kappa = \frac{\beta}{2} \frac{n}{m} \int \frac{d\epsilon}{2} \frac{\epsilon^2}{\Gamma} \text{sech}^2\left(\frac{1}{2}\beta E\right). \quad (5.34)$$

The ratio of the electronic thermal conductivities in superconducting and normal substances, when the conductivity is limited by phonon scattering, therefore reduces to

$$\frac{\kappa^S}{\kappa^N} = \frac{3}{2\pi^2} \int_0^\infty d\epsilon \epsilon^2 \text{sech}^2\left\{\frac{1}{2}[\epsilon^2 + (\beta\Delta)^2]^{\frac{1}{2}}\right\}. \quad (5.35)$$

This ratio is based on a model in which the interactions which lead to a lifetime for single-particle excitations are included by inserting a parameter Γ into the single-particle correlation functions. If these correlation functions were expressed as functions of space and time and substituted into the current correlation functions, their essential effect would be to reduce that correlation function by the factor $\exp(-\Gamma|t-t'|)$. This modification agrees with our expectation that phonon emission and absorption is naturally described by a relatively constant lifetime. The effects of impurity scattering, on the other hand, are better described by a mean free path which is relatively constant over a wide range of group velocities. This mean free path effect has been discussed extensively by Abrikosov and Gor'kov.⁴ It leads to current correlation functions which are modified by the factor $\exp(-|\mathbf{r}-\mathbf{r}'|/l)$. In computing the thermal conductivity in the presence of impurity scattering, it is therefore necessary to multiply the correlation functions previously introduced by this factor. The thermal conductivity then becomes

$$T\kappa = \frac{\beta n}{2m} \int d\mathbf{r} \exp\left(-\frac{r}{l}\right) \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot \mathbf{r}} \int d\epsilon \epsilon^2 \int \frac{d\omega'}{2\pi} \int_{-1}^{+1} \frac{dz}{2}$$

$$\times \text{Re}[G(\epsilon_+, \omega') G(\epsilon_-, \omega') + F(\epsilon_+, \omega') F(\epsilon_-, \omega')]. \quad (5.37)$$

When the forms for F and G which include Γ are inserted

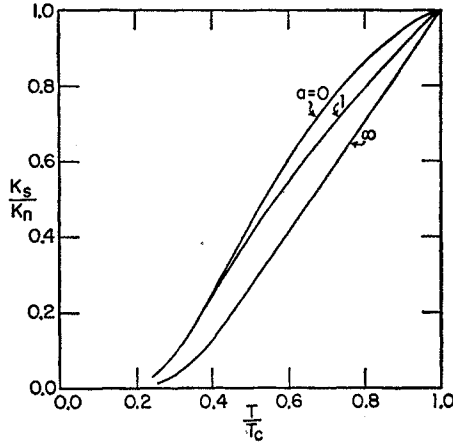


FIG. 2. Ratio of thermal conductivities in superconducting and normal states as a function of reduced temperature. The parameter a is the ratio of the thermal resistance resulting from phonons to the resistance due to impurities at the critical temperature. This parameter is effectively zero in alloys and other impure materials. It can be determined from the temperature dependence of the thermal conductivity in the normal state.

into the equation for the thermal conductivity and Γ and v_F/l are taken to be smaller than Δ and β^{-1} , we obtain

$$T_K = \frac{\beta n}{2m} \int d\mathbf{r} \exp\left(-\frac{r}{l}\right) \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k} \cdot \mathbf{r}} \int \frac{d\epsilon}{2} \epsilon^2 \operatorname{sech}^2\left(\frac{1}{2}\beta E\right) \times \int_0^1 dz \frac{\Gamma}{\Gamma^2 + (k\epsilon v_F z/E)^2}. \quad (5.38)$$

Since the \mathbf{k} integration is the transform of a Yukawa potential, we have

$$T_K = \frac{\beta n}{2m} \int dr \exp\left(-\frac{r}{l}\right) \int \frac{d\epsilon}{2} \epsilon^2 \operatorname{sech}^2\left(\frac{1}{2}\beta E\right) \times \int_0^1 dz \exp\left(-\frac{E\Gamma r}{\epsilon v_F z}\right) \frac{\Gamma}{4\pi r} \left(\frac{E}{\epsilon v_F z}\right)^2. \quad (5.39)$$

The z integration yields

$$T_K = \frac{\beta n}{2m} \int_0^\infty dr \int_0^\infty d\epsilon \epsilon^2 (E/\epsilon v_F) \operatorname{sech}^2\left(\frac{1}{2}\beta E\right) \times \exp[-r(1/l + E\Gamma/\epsilon v_F)]. \quad (5.40)$$

Finally, the integration over r is performed,

$$T_K = \frac{\beta n}{2m} \int_0^\infty d\epsilon \epsilon^2 \operatorname{sech}^2\left(\frac{1}{2}\beta E\right) [\Gamma + v_F \epsilon/E]^{-1}. \quad (5.41)$$

This equation for the thermal conductivity has several interesting features. In the normal metal ϵ and E are

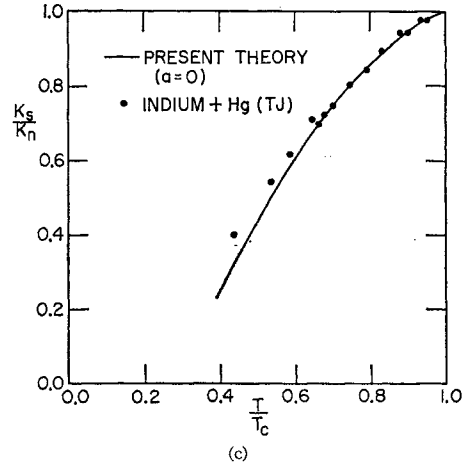
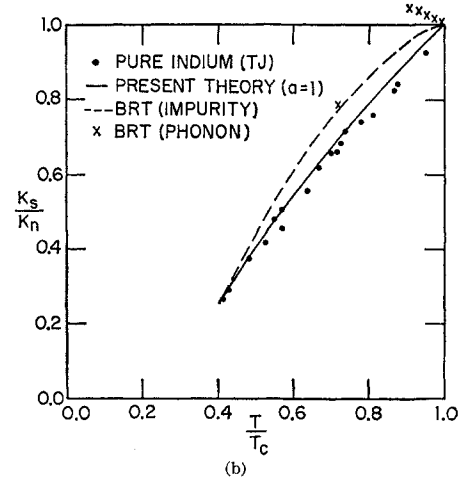
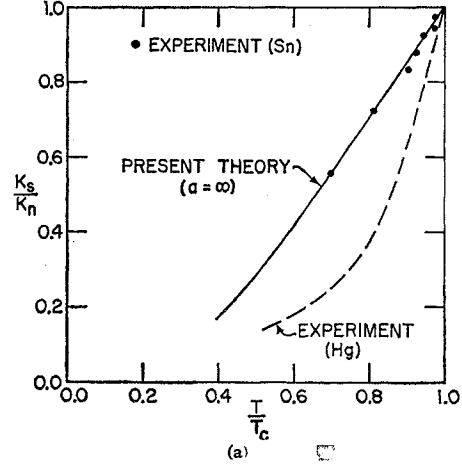


FIG. 3. (a) Comparison of theory and experiment for extremely pure metals. The recent data of Guenault for very pure tin agree very well with the theory; the data on mercury remain unexplained. In mercury, however, the condition $\beta\Gamma \ll 1$ is not well fulfilled. (b) Comparison of theory and experiment for metals of intermediate impurity. The thermal conductivity in a sample of indium which had equal amounts of impurity and phonon resistance at the critical temperature was measured by Toxen and Jones. The present theory is compared with their experimental

identical so that the thermal conductivity reduces to

$$\kappa^N = \frac{\pi^2}{3} \frac{n}{m} k_B^2 T [\Gamma + v_F/l]^{-1}. \quad (5.42)$$

The two contributions to the thermal resistance— Γ , which results from phonon absorption and emission and is proportional to T^3 , and v_F/l , which results from impurity scattering and is independent of temperature—contribute additively to the thermal resistance. This additivity is well verified experimentally. When there is very little impurity scattering and v_F/l is much smaller than Γ , Eq. (5.41) reduces to the expression (5.34) which describes thermal conductivity limited by phonon-electron interaction. On the other hand, when impurity scattering predominates, the thermal conductivity of a superconductor becomes

$$\kappa^S = \frac{n}{2m} \frac{\beta}{T} \frac{l}{v_F} \int_0^\infty d\epsilon \epsilon E \operatorname{sech}^2(\frac{1}{2}\beta E). \quad (5.43)$$

This expression has been obtained by Bardeen and co-workers²⁴ and is in close agreement with experiments on impure superconductors. More generally, the ratio of the thermal conductivity in normal and superconducting states can be written as

$$\frac{\kappa^S}{\kappa^N} = \frac{3\beta^3}{2\pi^2} \int_0^\infty d\epsilon \epsilon^2 \operatorname{sech}^2(\frac{1}{2}\beta E) \frac{1 + (v_F/l\Gamma)}{1 + (v_F\epsilon/E\Gamma)}. \quad (5.44)$$

If we assume that l is independent of T and Γ is proportional to T^3 , it is possible to express the temperature dependence of the ratio (κ^S/κ^N) in terms of a single parameter, a , which measures the ratio of the lattice thermal resistance to the impurity resistance at the critical temperature. In terms of this parameter, the thermal conductivity ratio becomes

$$\frac{\kappa^S}{\kappa^N} = \frac{3}{2\pi^2} \int_0^\infty d\epsilon \epsilon^2 \operatorname{sech}^2\{\frac{1}{2}[\epsilon^2 + (\beta\Delta)^2]^{\frac{1}{2}}\} \times \left[1 + a \left(\frac{T}{T_c} \right)^3 \right] \left[\frac{\epsilon}{[\epsilon^2 + (\beta\Delta)^2]^{\frac{1}{2}}} + a \left(\frac{T}{T_c} \right)^3 \right]^{-1}. \quad (5.45)$$

In Figs. (2) and (3) this ratio of the conductivities is plotted as a function of temperature and compared with

points. The results of BRT are also depicted. The curve labeled "impurity" refers to the ratio of conductivities BRT predict when impurity resistance predominates; the points labeled "phonon" represent their lower limit on κ^S/κ^N when phonon emission and absorption is the principal source of resistance. (c) Comparison of theory and experiment for impure metals. The present discussion agrees with BRT when impurity resistance predominates. The experimental results are in accord with their predictions. The depicted measurements for indium with a small (London) A204, 98 (1950).

previous calculations and experiments on extremely and moderately pure superconductors.²⁵⁻²⁸

ACKNOWLEDGMENTS

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APPENDIX

To evaluate the integrals describing the transverse response we note that the main contribution comes from a thin shell in the neighborhood of the Fermi surface where the magnitude of the vector k' is approximately equal to p_F . We therefore write

$$\omega \sigma^{T++}(k^2 \omega^2) \coth \frac{1}{2} \beta \omega + i \nu^{T++}(k^2 \omega^2) = \frac{n e^2}{m} \int_{-\omega_D}^{\omega_D} d\epsilon \int_{-1}^1 \frac{dz}{2} \int \frac{d\omega'}{2\pi} \frac{3}{2} (1-z^2) \times G(\epsilon_+ \omega_+) G(\epsilon_- \omega_-), \quad (A.1)$$

$$\omega \sigma^{T+-}(k^2 \omega^2) \coth \frac{1}{2} \beta \omega + i \nu^{T+-}(k^2 \omega^2) = \frac{n e^2}{m} \int_{-\omega_D}^{\omega_D} d\epsilon \int_{-1}^1 \frac{dz}{2} \int \frac{d\omega'}{2\pi} \frac{3}{2} (1-z^2) \times F(\epsilon_+ \omega_+) F(\epsilon_- \omega_-), \quad (A.2)$$

where $\epsilon_\pm = \epsilon \pm \frac{1}{2} k v_F z$ and $\mathbf{k} \cdot \mathbf{k}' = p_F k z$. It is most convenient to perform the z integration after evaluating the functions

$$I^{++}(z, \omega) = \int d\epsilon \int \frac{d\omega'}{2\pi} G(\epsilon_+ \omega_+) G(\epsilon_- \omega_-), \quad (A.3)$$

$$I^{+-}(z, \omega) = \int d\epsilon \int \frac{d\omega'}{2\pi} F(\epsilon_+ \omega_+) F(\epsilon_- \omega_-).$$

or more explicitly the integrals²⁹

$$I^{\pm\pm}(z, \omega) = \int d\epsilon \int \frac{d\omega'}{2\pi} \left[P \frac{1}{\omega_+^2 - E_+^2} - \pi i \delta(\omega_+^2 - E_+^2) \tanh \frac{1}{2} \beta E_+ \right] \times \left[P \frac{1}{\omega_-^2 - E_-^2} - \pi i \delta(\omega_-^2 - E_-^2) \tanh \frac{1}{2} \beta E_- \right] J^{\pm\pm}, \quad (A.4)$$

²⁵ The work on thermal conductivity in pure samples, including Fig. 5(a) has been previously reported; L. P. Kadanoff and P. C. Martin, Bull. Am. Phys. Soc. 5, 13 (1960).

²⁶ A. M. Guenault, International Conference on Superconductivity, Cambridge, June, 1959 (unpublished).

²⁷ A. M. Toxen and R. E. Jones, Bull. Am. Phys. Soc. 5, 14 (1960). We are grateful to these authors for providing us with reproductions of the experimental plots they presented.

²⁸ The mercury data are due to J. K. Hulm, Proc. Roy. Soc. (London) A204, 98 (1950).

²⁹ The reader will note that the imaginary part of (A.4) is the same as the imaginary of Y in (4.41) with q_0 replaced by ω .

where $E_{\pm} = +[\epsilon_{\pm}^2 + \Delta^2]^{\frac{1}{2}}$, $J^{++} = (\omega_+ + \epsilon_+)(\omega_- + \epsilon_-)$, and $J^{+-} = \Delta^2$. We shall confine ourselves to determining the real part of the polarizability in the static limit. For this purpose it is only necessary to evaluate the imaginary part of the functions I :

$$\begin{aligned} \text{Im} I^{++}(z) = & - \int d\epsilon \int \frac{d\omega'}{2} (\omega'^2 + \epsilon_+ \epsilon_-) \\ & \times \left[\frac{1}{\omega'^2 - E_-^2} \delta(\omega'^2 - E_+^2) \tanh \frac{1}{2} \beta E_+ \right. \\ & \left. + \frac{1}{\omega'^2 - E_+^2} \delta(\omega'^2 - E_-^2) \tanh \frac{1}{2} \beta E_- \right]. \quad (\text{A.5}) \end{aligned}$$

We have omitted from (A.5) the terms odd in ϵ and ω' which vanish on integration. Performing the ω' integration we obtain

$$\begin{aligned} \text{Im} I^{++}(z) = & - \int d\epsilon \frac{1}{E_+^2 - E_-^2} \\ & \times \left[\frac{E_+^2 + \epsilon_+ \epsilon_-}{2E_+} \tanh \frac{1}{2} \beta E_+ - \frac{E_-^2 + \epsilon_+ \epsilon_-}{2E_-} \tanh \frac{1}{2} \beta E_- \right]. \quad (\text{A.6}) \end{aligned}$$

Correspondingly, the imaginary part of $I^{+-}(z)$ reduces to

$$\begin{aligned} \text{Im} I^{+-}(z) = & - \int d\epsilon \frac{\Delta^2}{E_+^2 - E_-^2} \left[\frac{\tanh \frac{1}{2} \beta E_+}{2E_+} - \frac{\tanh \frac{1}{2} \beta E_-}{2E_-} \right]. \quad (\text{A.7}) \end{aligned}$$

We may write the difference between (A.6) and (A.7) in the form

$$\begin{aligned} \text{Im}[I^{++}(z) - I^{+-}(z)] = & - \int d\epsilon \left[\frac{\epsilon_+}{\epsilon_+ - \epsilon_-} \frac{\tanh \frac{1}{2} \beta E_+}{2E_+} - \frac{\epsilon_-}{\epsilon_+ - \epsilon_-} \frac{\tanh \frac{1}{2} \beta E_-}{2E_-} \right] \quad (\text{A.8}) \end{aligned}$$

and evaluate the integral by observing that the contribution from small ϵ cancels identically. Replacing the integrand by its value for large ϵ we deduce that for $kv_F \ll \omega_D$

$$\begin{aligned} \text{Im}[I^{++}(z) - I^{+-}(z)] = & - \int_{-\omega_D}^{\omega_D} \frac{d\epsilon}{2kv_F z} \left[\frac{\epsilon_+}{E_+} - \frac{\epsilon_-}{E_-} \right] = -1. \quad (\text{A.9}) \end{aligned}$$

We may therefore write ν^{T++} and ν^{T+-} in the form

$$\begin{aligned} \nu^{T++}(k^2, 0) = & -(ne^2/m) [1 - \frac{1}{2} S_T(k^2)], \\ \nu^{T+-}(k^2, 0) = & (ne^2/2m) S_T(k^2), \quad (\text{A.10}) \end{aligned}$$

where

$$\begin{aligned} S_T(k^2) = & - \int_{-1}^{+1} \frac{dz}{2} (1 - z^2) \int d\epsilon \frac{\Delta^2}{E_+^2 - E_-^2} \\ & \times \left[\frac{\tanh \frac{1}{2} \beta E_+}{E_+} - \frac{\tanh \frac{1}{2} \beta E_-}{E_-} \right]. \quad (\text{A.11}) \end{aligned}$$

If we write $S_T(k^2) = \frac{3}{2} S_T^{(0)}(k^2) - \frac{1}{2} S_T^{(2)}(k^2)$, where $S_T^{(2)}(k^2)$ is the term involving z^2 ,

$$\begin{aligned} S_T^{(2)}(k^2) = & - \Delta^2 \int_{-1}^{+1} dz \\ & \times 3z^2 \int d\epsilon \frac{\tanh \frac{1}{2} \beta E}{E} \frac{1}{\epsilon^2 - (\epsilon - kv_F z)^2}, \quad (\text{A.12}) \end{aligned}$$

and integrate with respect to z , we obtain

$$\begin{aligned} S_T^{(2)}(k^2) = & \frac{6\Delta^2}{(kv_F)^2} \int d\epsilon \frac{\tanh \frac{1}{2} \beta E}{E} \\ & \times \left[1 - \frac{\epsilon}{kv_F} \ln \left| \frac{\epsilon + \frac{1}{2} kv_F}{\epsilon - \frac{1}{2} kv_F} \right| \right]. \quad (\text{A.13}) \end{aligned}$$

We note that in the limit in which $k \rightarrow 0$, this reduces to

$$\begin{aligned} S_T^{(2)}(0) = & - \Delta^2 \int \frac{d\epsilon}{2E} \frac{\partial}{\partial E} \frac{\tanh \frac{1}{2} \beta E}{E} \\ = & 1 - \int_0^\infty d\epsilon \frac{\partial}{\partial E} (\tanh \frac{1}{2} \beta E), \quad (\text{A.14}) \end{aligned}$$

which approaches unity as the temperature vanishes. Likewise the term in (A.11) which involves no z^2 , $S_T^{(0)}(k^2)$, can be expressed in a form convenient for treating its singularity at $z=0$ and $k=0$.

$$\begin{aligned} S_T^{(0)}(k^2) = & - \Delta^2 \tanh \frac{1}{2} \beta \Delta \\ & \times \int d\epsilon \int_{-1}^{+1} \frac{dz}{2} \frac{1}{(E_+^2 - E_-^2)} \left[\frac{1}{E_+} - \frac{1}{E_-} \right] \\ & + 2\Delta^2 \int d\epsilon \int_{-1}^{+1} \frac{dz}{2} \frac{1}{(E_+^2 - E_-^2)} \frac{1}{E_+} \\ & \times (\tanh \frac{1}{2} \beta \Delta - \tanh \frac{1}{2} \beta E_+). \quad (\text{A.15}) \end{aligned}$$

To evaluate the first term we observe that its integrand is regular everywhere. It is convenient to write its denominator $E_+^2 - E_-^2 = 2\epsilon kv_F z$ in the form $4(\epsilon - i\delta_1)(\frac{1}{2} kv_F z - i\delta_2)$, where δ_1 and δ_2 are real numbers, and let δ_1 and δ_2 approach zero. We may then translate the z variable so that the square-root factors depend only on the new variable $\epsilon' = \epsilon \pm \frac{1}{2} kv_F z$ and interchange orders

of integration, obtaining from the first term

$$\frac{-\Delta^2 \tanh \frac{1}{2} \beta \Delta}{4kv_F} \int_{-\infty}^{\infty} \frac{d\epsilon'}{\epsilon' - i\delta_2} \int_{\epsilon' - \frac{1}{2}kv_F}^{\epsilon' + \frac{1}{2}kv_F} d\epsilon \\ \times \left[\frac{1}{\epsilon - i\delta_1} + \frac{1}{\epsilon + i\delta_1} + \frac{2}{\epsilon' - \epsilon - i\delta_2} \right] \frac{1}{(\epsilon'^2 + \Delta^2)^{\frac{1}{2}}}.$$

When the ϵ integration is performed and $\delta_1 \rightarrow 0$, this expression reduces to

$$\frac{-\Delta \tanh \frac{1}{2} \beta \Delta}{2kv_F} \int_{-\infty}^{\infty} \frac{d\epsilon'}{\epsilon' - i\delta_2} \\ \times \left[\ln \left| \frac{\epsilon' + \frac{1}{2}kv_F}{\epsilon' - \frac{1}{2}kv_F} \right| + 2i \tan^{-1} \left(\frac{1}{\delta_2} \right) \right] \frac{1}{(\epsilon'^2 + \Delta^2)^{\frac{1}{2}}} \\ = \frac{\pi^2 \Delta}{2kv_F} \tanh \frac{1}{2} \beta \Delta - \frac{\Delta^2 \tanh \frac{1}{2} \beta \Delta}{kv_F} \int_0^{\infty} \frac{d\epsilon}{\epsilon E} \ln \left| \frac{\epsilon + \frac{1}{2}kv_F}{\epsilon - \frac{1}{2}kv_F} \right|.$$

The z integration of the second term of (A.15) can be performed by elementary methods and the terms combined with the result

$$S_T^{(0)}(k^2) = \frac{\pi^2 \Delta}{2kv_F} \tanh \frac{1}{2} \beta \Delta \\ - \frac{\Delta^2}{kv_F} \int_0^{\infty} \frac{d\epsilon}{\epsilon E} \ln \left| \frac{\epsilon + \frac{1}{2}kv_F}{\epsilon - \frac{1}{2}kv_F} \right| \tanh \frac{1}{2} \beta E. \quad (\text{A.16})$$

As the induced motional current is related to the external potential, the induced spin magnetization is determined from

$$\langle \mathbf{M}(1) \rangle = i \int_{-\infty}^0 \mu_e^2 \langle [n^+(1) - n^-(1), n^+(2) - n^-(2)]_R \rangle \\ \times \mathbf{H}(2) d2, \quad (\text{A.17})$$

where μ_e is the electron magnetic moment and $\mathbf{H}(\mathbf{r})$ the magnetic field. The spin susceptibility is then expressed in terms of the Fourier transform of the commutator of the net spin density operator,

$$\mu_e^2 \langle [n^+(1) - n^-(1), n^+(2) - n^-(2)] \rangle \\ = \int \frac{d\omega}{\pi} \int \frac{d\mathbf{k}}{(2\pi)^3} \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2) - i\omega(t_1 - t_2)] \\ \times \omega \gamma_{sp}(k^2 \omega^2) \quad (\text{A.18})$$

as the integral

$$\chi_{sp}(k^2 \omega^2) = -\frac{2}{\pi} \int_0^{\infty} d\omega' P \frac{\omega'^2}{\omega'^2 - \omega^2} \gamma_{sp}(k^2 \omega'^2). \quad (\text{A.19})$$

Using the relation between the commutator and the imaginary part of the Green's function, and the connection between the retarded commutator and the susceptibility, we write

$$\chi_{sp}(k^2 0) = \mu_e^2 \int_{-\infty}^0 dt_1 \int d\mathbf{r}_1 e^{i\mathbf{k} \cdot \mathbf{r}_1} \\ \times 4 \operatorname{Im} [G^{++}(12; 1+2^+) - G^{+-}(12; 1+2^+)]_{\mathbf{r}_2 = t_2 = 0}. \quad (\text{A.20})$$

In a normal metal, this integral reduces to the familiar result $\chi_{sp}^N = \mu_e m p_F / \pi^2$. In a superconductor, the calculation in terms of the Green's functions derived in Sec. 2 involves the same integral $S_T^{(0)}$ evaluated above. Consequently, the susceptibility reduces to

$$\chi_{sp}(k^2 0) = (\mu_e^2 m p_F / \pi^2) [1 - S_T^{(0)}(k^2)]. \quad (\text{A.21})$$