Theory of the Electronic Thermal Conductivity of Superconductors with Strong Electron-Phonon Coupling

VINAY AMBEGAOKAR*

Department of Physics and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

AND

LUDWIG TEWORDT

Bell Telephone Laboratories, Murray Hill, New Jersey (Received 7 October 1963; revised manuscript received 13 January 1964)

The electronic thermal conductivity of superconductors is discussed without recourse to the quasiparticle approximation. The Kubo formula for the thermal conductivity is used as the starting point. This is first examined in the Hartree-Fock approximation in the Nambu space. It is shown that in the Eliashberg approximation of neglecting the momentum dependence of the electronic self-energy, the calculation of the thermal conductivity is reduced to a quadrature, involving however the complex energy gap and renormalization functions which are solutions of the Eliashberg gap equations at finite temperatures. These equations are given in an Appendix. The problem is also considered in the ladder approximation in the Nambu space, and a generalized Boltzmann equation is derived which includes corrections to the Hartree-Fock approximation corresponding to the replacement of the scattering by the transport cross section. It is shown that the standard Boltzmann equation for superconducting quasiparticles is obtained in the weak-coupling limit. No numerical calculations are performed in this paper, but a clear scheme for such calculations is outlined. Reasons for believing that such calculations will explain the anomalous drop in the electronic thermal conductivity of superconducting lead are given.

I. INTRODUCTION

EXPERIMENTS on the strong elemental superconductors lead and mercury show that the electronic thermal conductivity of these materials differs markedly from that of typical weak superconductors like tin or indium. For lead and mercury¹ the ratio, K_s/K_n , of the thermal conductivity in the superconducting and normal states when plotted against the reduced temperature T/T_c shows a steep positive slope of about 5 near $T=T_c$. For tin² and indium,³ on the other hand, the experiments yield a smaller slope of about 1.6.

A theory of the electronic thermal conductivity of superconductors based on the quasiparticle approximation and the Boltzmann equation approach of Bardeen, Rickayzen, and one of the present authors⁴ has been carried through previously.⁵ The results obtained are in substantial agreement with the data on tin and indium. The lack of agreement between the theory given in I and the data on lead is not surprising since, as shown in

the work of Schrieffer, Scalapino, and Wilkins,⁶ the strong electron-phonon coupling causes the quasiparticle picture to be quite meaningless over much of the energy spectrum.

It therefore seems reasonable to study the thermal conductivity of lead on the basis of the strong-coupling theory used by Schrieffer *et al.*⁶ in explaining tunneling characteristics. This is the aim of the present paper. We use the method of thermodynamic Green's functions⁷ and thereby avoid the quasiparticle approximation. We expect that in the limit of almost stable excitations our theory will reduce to the theory developed in I, and this expectation is realized. In this paper we carry the theory as far as we are able to without using numerical methods. We expect to use the formulas obtained here as the basis for further calculation.

Our starting point is the Kubo formula in which the thermal conductivity is expressed in terms of the correlation function of two heat current operators. For the superconducting state it is convenient to use the two component space introduced by Nambu. In Sec. II the problem is treated in the Hartree-Fock approximation which means that the correlation function is factored into two Nambu matrix Green's functions. The momentum integration in the expression for the thermal

^{*} Alfred P. Sloan Foundation Fellow.

[†]Permanent address: Institut für Angewandte Physik, Universität Hamburg, Hamburg, Germany.

¹ J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1956); J. H. P. Watson and G. M. Graham, Can. J. Phys. **41**, 1738 (1963).

² A. M. Guenault, Proc. Roy. Soc. (London) A262, 420 (1961).

<sup>A. M. Toxen and R. E. Jones, Phys. Rev. 120, 1167 (1960).
J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. 113, 982 (1959).</sup>

⁵ L. Tewordt, Phys. Rev. **129**, 657 (1963), hereafter referred to as I. Other work on this subject is contained in L. Tewordt, *ibid*. **128**, 12 (1962), hereafter referred to as II; L. P. Kadanoff and P. Martin, *ibid*. **124**, 678 (1961); B. T. Geilikman, V. Z. Kresin, Zh. Eksperim. i Teor. Fiz. **41**, 1142 (1961) [English transl.: Soviet Phys.—JETP **14**, 816 (1962)].

 $^{^6}$ J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters $\bf 10,\,336\,\,(1963).$

⁷ Several references on the Green's function method are now available. A reference in which the treatment is similar in style and notation to that of the present paper is V. Ambegaokar, 1962 Brandeis Lectures (W. A. Benjamin, Inc., New York, 1963), Vol. 2. Other references are given here.

 $^{^8\,\}mathrm{We}$ use the form given by J. S. Langer, Phys. Rev. 128, 110 (1962). See also Ref. 7.

⁹ Y. Nambu, Phys. Rev. 117, 648 (1960).

conductivity can be carried out if one makes the weak-momentum approximation introduced by Eliashberg, 10 that is, if one neglects the p dependence of the renormalization function $Z_p(\omega)$ and the gap function $\Delta_p(\omega)$. In contrast to the result of the quasiparticle approach, the thermal conductivity is expressed as an integral over all excitation energies rather than over all momenta. The integrand contains the complex functions $Z(\omega)$ and $\Delta(\omega)$. These functions have to be determined from the generalization to finite temperatures of Eliashberg's gap equations. The generalized gap equations are given in Appendix A. In the limit of zero temperature these equations have been solved for lead by Schrieffer et al. However, for the problem of the thermal conductivity one needs the solutions near T_c .

In Sec. III the problem is treated in the more general ladder approximation in the Nambu space. This is the approximation that must be used with the superconducting approximation to the single-particle selfenergy operator in order to preserve conservation laws¹¹ or, equivalently, Ward identities. To facilitate the treatment of this approximation we use a method introduced recently by Langer, Maradudin, and Wallis¹² in discussing optical absorption by anharmonic crystals. The integral equation for the vertex part is simplified by using a double spectral representation (derived in Appendix B) for the vertex function. The resulting integral equation for one of the spectral functions corresponds to a generalized Boltzmann equation in which this function essentially plays the role of the nonequilibrium part of the distribution function. The integral equation simplifies if one makes an Ansatz for the vector part of the spectral function which corresponds to Bloch's Ansatz in the elementary theory, and further, if one again uses the weak-momentum approximation. In this way one obtains an integral equation in the energy variable alone which represents the generalization of Bloch's equation for thermal conductivity to a strongly coupled superconductor. In the limit of weak electron-phonon interaction the equation reduces to the Boltzmann equation used in I.

II. HARTREE-FOCK APPROXIMATION

If we neglect the entropy flow and measure energies with respect to the chemical potential, 13 the Kubo formula for the thermal conductivity K may be written as follows (we use units in which $\hbar = 1$):

$$K = \frac{2}{3VT} \operatorname{Im} \int_{-\infty}^{0} dt_2 t_2 \int d^3 x_1 d^3 x_2 \langle \mathbf{u}(\mathbf{x}_1, 0) \cdot \mathbf{u}(\mathbf{x}_2, t_2) \rangle. \tag{2.1}$$

Above V is the volume of the system, T is the temperature, and \mathbf{u} is the heat-current density operator at the space-time point $1=(\mathbf{x}_1,t_1)$. The brackets denote an average in the grand canonical ensemble. For the interacting electron-phonon system \mathbf{u} has the form $\mathbf{u}=\mathbf{u}_{\rm el}+\mathbf{u}_{\rm ph}$, where

$$\mathbf{u}_{\text{el}} = -\frac{1}{2m} \sum_{\sigma} \left(\frac{\partial}{\partial t_1} \nabla_1' + \frac{\partial}{\partial t_1'} \nabla_1 \right) \psi_{\sigma}^{\dagger}(1') \psi_{\sigma}(1) |_{1'=1} \quad (2.2)$$

is the heat current for the electronic system. It includes that part of the electron-phonon interaction energy which is due to electronic charge fluctuations. [The operators $\psi_{\sigma}^{\dagger}(1')$ and $\psi_{\sigma}(1)$ create and annihilate electrons with spin σ at 1' and 1, respectively.]

The detailed form of the phonon part of the heatcurrent density operator¹⁴ is not needed for the purposes of this paper. It suffices to note that the correlation function of \mathbf{u}_{ph} with itself gives rise through Eq. (2.1) to a thermal conductivity which may be interpreted as the thermal conductivity of the lattice as limited by electron scattering.15 In the normal state this contribution is proportional to T^2 and is too small to be observed in a pure system. In the superconducting state the lattice thermal conductivity is increased relative to that in the normal state because the energy gap in the electronic spectrum leads to an increase in the relaxation time for phonons. However, because of the smallness of the lattice term, the electronic contribution (though rapidly falling) will dominate the thermal conductivity just below T_c which is the region of interest to us. The cross terms in the expression (2.1) between \mathbf{u}_{el} and \mathbf{u}_{ph} describe "phonon drag" effects which are totally negligible for heat conduction because the electronic heat current is odd with respect to reflections in the Fermi surface. In what follows, therefore, we take (2.2) as the expression for the heat current operator and drop the subscript "el." In the language of conventional transport theory we are assuming that the lattice is always in equilibrium. The contribution to the thermal conductivity of the processes by which the lattice does in fact achieve equilibrium are, as we have seen, small in the region of interest to us.

Let us introduce the correlation function

$$P(1,2) = \langle T \lceil \mathbf{u}(1) \cdot \mathbf{u}(2) \rceil \rangle, \qquad (2.3)$$

where T is Wick's time ordering operator. In the standard way we make Fourier transformations in the spatial and imaginary time difference coordinates, so

¹⁰ G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. 38, 960 (1960) [English transl. Soviet Phys.—JETP 9, 1385 (1959)].

¹¹ G. Baym and L. P. Kadanoff, Phys. Rev. 124, 287 (1961).

¹² J. S. Langer, A. A. Maradudin, and R. F. Wallis, Proceedings of the International Conference on Lattice Dynamics, 1963 (to be published).

¹³ See L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) 24, 419 (1963), for a discussion of this point.

¹⁴ In a continuum Debye approximation this has the form given by K. Baumann, Ann. Phys. (N. Y.) 23, 221 (1963).

by K. Bathham, Ahh. Thys. (N. 1.) 23, 221 (1905). Is Because the phonon lifetimes contain the small quantity $(m/M)^{1/2}$ where M is the ionic mass, the quasiparticle approximation is valid for the phonons. {See Ref. 10 and A. B. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 1438 (1958) [English transl.: Soviet Phys.—JETP 14, 816 (1962)].} By using the methods of the present paper one can recover a Boltzmann equation for the thermal conduction by phonons as limited by electron scattering.

that

$$P(1,2) = \int \frac{d^{3}q}{(2\pi)^{3}} \frac{i}{\beta} \sum_{\nu_{m}} P(q,\nu_{m}) \times \exp\{i[\mathbf{q} \cdot (\mathbf{x}_{1} - \mathbf{x}_{2}) - \nu_{m}(t_{1} - t_{2})]\}. \quad (2.4)$$

Here $\nu_m = 2\pi mi/\beta$, m runs over all integers, and $\beta = (k_B T)^{-1}$ with k_B Boltzmann's constant. In terms of $P(q,\nu_m)$ Eq. (2.1) becomes

$$K = -\frac{1}{3T} \frac{d}{d\nu} \{ \text{Re}[P(q,\nu_m)|_{\nu_m = \nu - i0^+}] \} \Big|_{\substack{\nu = 0 \\ q = 0}}. \quad (2.5)$$

It is convenient to use Nambu's two-component field operators defined by

$$\psi(1) = \begin{pmatrix} \psi_{\uparrow} & (1) \\ \psi_{\downarrow\uparrow} \uparrow & (1) \end{pmatrix}, \quad \psi^{\dagger}(1) = (\psi_{\uparrow} \uparrow (1) \psi_{\downarrow} (1)).$$

In terms of these and the Pauli spin matrices τ_i the correlation function may be written as follows

$$P(1,2) = \frac{1}{4m^2} \left(\frac{\partial}{\partial t_1} \nabla_1' + \frac{\partial}{\partial t_1'} \nabla_1 \right)$$

$$\cdot \left(\frac{\partial}{\partial t_2} \nabla_2' + \frac{\partial}{\partial t_2'} \nabla_2 \right) (\tau_3)^{ij} (\tau_3)^{kl}$$

$$\times \left\langle T \left[\psi_i(1) \psi_k(2) \psi_l^{\dagger}(2') \psi_j^{\dagger}(1') \right] \right\rangle \Big|_{\substack{1' = 1^+ \\ 2' = 2^+}}. \tag{2.6}$$

In writing the correlation function in the form (2.6) we have neglected certain discontinuity terms that arise from the time derivatives acting on the time ordering operator. These terms make no contribution to the thermal conductivity.

In this section we shall derive the expression for K in the Hartree-Fock approximation. This is defined by

$$\langle T \lceil \psi_i(1)\psi_k(2)\psi_l^{\dagger}(2')\psi_i^{\dagger}(1') \rceil \rangle \rightarrow g_{il}(12')g_{ki}(21'), \quad (2.7)$$

where g_{il} is Nambu's matrix Green's function

$$g_{il}(12) = -i \langle T[\psi_i(1)\psi_l^{\dagger}(2)] \rangle. \tag{2.8}$$

Then we obtain from Eqs. (2.6), (2.7), and (2.4)

$$P(q,\nu_m) = \frac{1}{4m^2} \int \frac{d^3p}{(2\pi)^3} \frac{i}{\beta} \sum_{\xi i} e^{\xi_{\ell} 0^+} [\zeta_{\ell}(\mathbf{p}+\mathbf{q}) + (\zeta_{\ell}+\nu_m)\mathbf{p}]^2$$

$$\times \operatorname{Tr} \{ \tau_3 \mathcal{G}(p+q, \zeta_1+\nu_m) \tau_3 \mathcal{G}(p,\zeta_1) \}, (2.9)$$

where $\zeta_l = (2l+1)\pi i/\beta$ and l takes on integral values. The Hartree-Fock approximation for the heat-current correlation function is represented by the diagram in Fig. 1.

We now insert the spectral representation for $\mathcal{G}(p,\zeta_l)$,

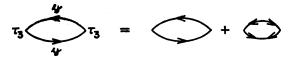


Fig. 1. Diagrammatic representation of the Hartree-Fock approximation for the heat-current correlation function of superconductors. The solid lines on the left of the equality sign represent Nambu matrix propagators $\mathfrak F$. The equivalent diagrammatic representation in terms of Gorkov's normal and anomalous Green's functions is shown on the right. In the present formalism the terms on the right arise from taking the trace $\mathrm{Tr}[\tau_3 \mathcal F_{\tau_3} \mathcal F_{\tau_3}]$.

namely,

$$g(p,\zeta_l) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{a(p,\omega)}{\zeta_l - \omega}$$
 (2.10)

into (2.9) and carry out the sum over ζ_l . Introducing the result into (2.5) one finds

$$K = \frac{1}{24m^2k_BT^2} \int \frac{d^3pd\omega}{(2\pi)^4} p^2\omega^2 \operatorname{sech}^2(\frac{1}{2}\beta\omega) \times \operatorname{Tr}\{\tau_3 a(p,\omega)\tau_3 a(p,\omega)\}. \quad (2.11)$$

The Nambu matrix propagator $g(p,\zeta_l)$ with ζ_l continued to the complete complex z plane has the form

$$G(p,z) = \frac{zZ_p(z) + \epsilon_p \tau_3 + \phi_p(z)\tau_1}{z^2 Z_p^2(z) - \epsilon_p^2 - \phi_p^2(z)}, \qquad (2.12)$$

where $\epsilon_p = (p^2/2m) - \mu$. The renormalization function $Z_p(z)$ and the gap function $\phi_p(z)$, both complex, have to be determined from the Nambu-Eliashberg self-consistency condition. We now make the weak-momentum approximation introduced by Eliashberg, that is we neglect the p dependence of $Z_p(z)$ and $\phi_p(z)$. Then the integration over p, or ϵ_p , in Eq. (2.11) can be done. The spectral function $a(p,\omega)$ is obtained from (2.12) from the relation

$$a(p,\omega) = 2 \operatorname{Im} g(p, \omega - i0^{+}) = (1/i) [g(p, \omega - i0^{+}) - g(p, \omega + i0^{+})].$$
 (2.13)

The integrals over ϵ that are then needed are

$$I_{1} = \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr} \{ \tau_{3} \mathcal{G}(p, \omega - i0^{+}) \tau_{3} \mathcal{G}(p, \omega - i0^{+}) \}$$

$$= 0, \qquad (2.14)$$

and

$$I_2 = \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr} \{ \tau_3 \mathcal{G}(p, \omega - i0^+) \tau_3 \mathcal{G}(p, \omega + i0^+) \}$$

$$= \frac{\pi}{|\operatorname{Im}\{Z(\omega)[\omega^{2} - \Delta^{2}(\omega)]^{1/2}\}|} \times \left(1 + \frac{\omega^{2} - |\Delta(\omega)|^{2}}{|\omega^{2} - \Delta^{2}(\omega)|}\right). \quad (2.15)$$

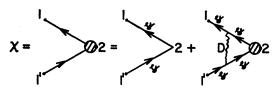


Fig. 2. Integral equation for the vertex function in the ladder approximation, represented in terms of diagrams. $\mathcal G$ and D denote particle and phonon propagators, respectively.

The integrations are straightforward and are sketeched in Appendix C. The complex functions $Z(\omega)$ and $\Delta(\omega)$, the latter being the complex energy gap parameter, are related to the functions occurring in (2.12) by

$$\begin{split} Z(\omega) &= Z_1(\omega) + i Z_2(\omega) = Z(z = \omega - i0^+); \\ \Delta(\omega) &= \Delta_1(\omega) + i \Delta_2(\omega) \\ &= \phi(z = \omega - i0^+) / Z(z = \omega - i0^+). \end{split} \tag{2.16}$$

The thermal conductivity K is now given by

$$K = \frac{n}{8mk_B T^2} \int_0^\infty d\omega \frac{\omega^2 \operatorname{sech}^2(\frac{1}{2}\beta\omega)}{|\operatorname{Im}\{Z(\omega)[\omega^2 - \Delta^2(\omega)]^{1/2}\}|} \times \left(1 + \frac{\omega^2 - |\Delta(\omega)|^2}{|\omega^2 - \Delta^2(\omega)|}\right). \quad (2.17)$$

Above n is the density of electrons. Near T=0 the factor in the large brackets becomes zero for $\omega < \Delta_0$, where $\Delta_0 = \Delta_1(\Delta_0)$ is the gap edge, since Δ_2 vanishes for $\omega < \Delta_0$. At finite temperatures the existence of thermally excited phonons may cause Δ_2 to have a small nonzero value for $\omega < \Delta_0$.

If for those frequencies ω that contribute predominantly to the integral in (2.17) the inequality $2\Delta_2\Delta_1<\omega^2-\Delta_1^2+\Delta_2^2$ is satisfied, the following approximate formula for K obtains

$$K = \frac{n}{8mk_B T^2} \int_0^\infty d\omega \frac{\omega^2 (\omega^2 - \Delta_1^2 + \Delta_2^2)^{1/2}}{|Z_2(\omega^2 - \Delta_1^2 + \Delta_2^2) - Z_1 \Delta_1 \Delta_2|} \times \operatorname{sech}^2(\frac{1}{2}\beta\omega) \left(1 + \frac{\omega^2 - \Delta_1^2 - \Delta_2^2}{|\omega^2 - \Delta_1^2 + \Delta_2^2|}\right). \quad (2.18)$$

To first order in Δ_2 and Z_2 the expression in the denominator of the integrand in (2.18) reduces to $\omega Z_1\Gamma$, where Γ is one-half the decay rate for a quasiparticle as calculated in II. Equation (2.18) is thus somewhat more general than the quasiparticle approximation. In the case of lead it would appear that the condition $\Delta_2\Delta_1 < \omega^2 - \Delta_1^2 + \Delta_2^2$ is reasonably well satisfied for frequencies below 2 or $3k_BT_c$, the latter being roughly the

frequency which contributes maximally to K, but in a numerical calculation it is probably no harder to use the exact form (2.17).

III. GENERALIZED BOLTZMANN EQUATION

We now wish to obtain a Boltzmann-like equation for the correlation function P(1,2). It is convenient first to rewrite the expression for this quantity as follows:

$$P(1,2) = \frac{1}{2m} \left(\frac{\partial}{\partial t_1} \nabla_1' + \frac{\partial}{\partial t_1'} \nabla \right) \cdot \text{Tr} \{ \tau_3 \chi(1,2,1') \} \big|_{1'=1^+}, \quad (3.1)$$

where the three-point function $\chi(1,2,1')$ is defined by

$$\chi_{ij} = \langle T[\psi_i(1)\mathbf{u}(2)\psi_j^{\dagger}(1')] \rangle. \tag{3.2}$$

[In writing (3.1) we have again neglected, for the same reason as given below Eq. (2.6), terms arising from the nonzero commutator of the time derivative and time-ordering operations.] Because of the homogeneity of space and time χ depends only on two space-time coordinate differences, so that $\chi = \chi(1-2,2-1')$. Since, furthermore, this quantity has periodicity properties along the imaginary time axis, one may make Fourier integral and series expansions in both space-time arguments. We shall denote the Fourier transform by $\chi(\mathbf{p}+\mathbf{q}, \zeta_l+\nu_m; \mathbf{p}, \zeta_l)$. Inserting the Fourier expansion for χ into (3.1) one obtains the following expression for $P(q,\nu_m)$:

$$P(q,\nu_m) = -\frac{1}{2m} \frac{i}{\beta} \sum_{\zeta_l} e^{\zeta_l 0^+} \int \frac{d^3 p}{(2\pi)^3} [(\zeta_l + \nu_m) \mathbf{p} + \zeta_l (\mathbf{p} + \mathbf{q})] \cdot \text{Tr} \{ \tau_3 \chi(\mathbf{p} + \mathbf{q}, \zeta_l + \nu_m; \mathbf{p}, \zeta_l) \}. \quad (3.3)$$

In Appendix B we have derived the following double spectral representation for χ (see also Ref. 12)

$$\chi(\mathbf{p}+\mathbf{q}, \zeta_{l}+\nu_{m}; \mathbf{p}, \zeta_{l}) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\omega_{1}d\omega_{2}}{(2\pi)^{2}} \left[\frac{\mathbf{f}^{(1)}(\mathbf{p}+\mathbf{q}, \omega_{1}; \mathbf{p}, \omega_{2})}{(\zeta_{l}-\omega_{1})(\nu_{m}-\omega_{2})} + \frac{\mathbf{f}^{(2)}(\mathbf{p}+\mathbf{q}, \omega_{1}; \mathbf{p}, \omega_{2})}{(\zeta_{l}+\nu_{m}-\omega_{1})(\nu_{m}-\omega_{2})} \right]. \quad (3.4)$$

The explicit forms of the spectral functions $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ are given in Appendix B. We insert Eq. (3.4) into Eq. (3.3), perform the sum over ζ_l , and introduce the result for $P(q,\nu_m)$ into (2.5). The result for K in terms of $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ is then found to be

$$K = \frac{1}{12mT} \int \frac{d^{3}p d\omega}{(2\pi)^{4}} \mathbf{p} \cdot \text{Tr} \left\{ \frac{1}{2}\beta\omega \operatorname{sech}^{2}(\frac{1}{2}\beta\omega)\tau_{3}\mathbf{f}_{\mathbf{p}}^{(2)}(\omega,0) - (e^{\beta\omega} + 1)^{-1} \left[\tau_{3}(\mathbf{f}_{\mathbf{p}}^{(1)}(\omega,0) + \mathbf{f}_{\mathbf{p}}^{(2)}(\omega,0)) + 2\omega\tau_{3}\frac{\partial}{\partial\nu}(\mathbf{f}_{\mathbf{p}}^{(1)}(\omega,\nu) + \mathbf{f}_{\mathbf{p}}^{(2)}(\omega+\nu,\nu)) |_{\nu=0} \right] \right\}. \quad (3.5)$$

Here we have used the abbreviation $\mathbf{f}_{\mathbf{p}}^{(i)}(\omega,\nu) = \mathbf{f}^{(i)}(\mathbf{p},\omega,\mathbf{p},\nu), i=1, 2.$

To proceed further we must determine the spectral functions $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ in some approximation. We consider the integral equation for χ in the ladder approximation which is represented by the diagrams in Fig. 2 and is given by

$$\chi(\mathbf{p}, \zeta_{l} + \nu_{m}; \mathbf{p}, \zeta_{l}) = -\frac{1}{2m} \mathbf{p}(2\zeta_{l} + \nu_{m}) \mathcal{G}(p, \zeta_{l} + \nu_{m}) \tau_{3} \mathcal{G}(p, \zeta_{l}) + \frac{1}{2m} \mathbf{p} \left[\mathcal{G}(p, \zeta_{l} + \nu_{m}) \tau_{3} + \tau_{3} \mathcal{G}(p, \zeta_{l}) \right]
- \frac{1}{\beta} \sum_{\mu_{n}} \int \frac{d^{3}k}{(2\pi)^{3}} \mathcal{G}(p, \zeta_{l} + \nu_{m}) \tau_{3} \chi(\mathbf{p} - \mathbf{k}, \zeta_{l} + \nu_{m} - \mu_{n}; \mathbf{p} - \mathbf{k}, \zeta_{l} - \mu_{n}) \tau_{3} \mathcal{G}(p, \zeta_{l}) D(\mathbf{k}, \mu_{n}).$$
(3.6)

Here $D(\mathbf{k},\mu_n)$ is the phonon propagator $(\mu_n=2\pi ni/\beta)$ with n an integer) which has the spectral representation

$$D(\mathbf{k},\mu_n) = \int_{-\infty}^{\infty} \frac{d\nu}{2\pi} \frac{d(k,\nu)}{\mu_n - \nu}.$$
(3.7)

Introducing this spectral representation as well as those for \mathfrak{F} and \mathfrak{T} into (3.6) and doing the sum over n we find

$$\int \frac{d\omega_{1}d\omega_{2}}{(2\pi)^{2}} \left[\frac{\mathbf{f}_{p}^{(1)}(\omega_{1},\omega_{2})}{(\zeta_{l}-\omega_{1})(\nu_{m}-\omega_{2})} + \frac{\mathbf{f}_{p}^{(2)}(\omega_{1},\omega_{2})}{(\zeta_{l}+\nu_{m}-\omega_{1})(\nu_{m}-\omega_{2})} \right] \\
= -\frac{\mathbf{p}}{2m} (2\zeta_{l}+\nu_{m}) \int \frac{d\omega_{1}d\omega_{2}}{(2\pi)^{2}} \frac{a(p,\omega_{1})\tau_{3}a(p,\omega_{2})}{(\zeta_{l}+\nu_{m}-\omega_{1})(\zeta_{l}-\omega_{2})} \\
+ \frac{\mathbf{p}}{2m} \left[\int \frac{d\omega_{1}}{2\pi} \left(\frac{a(p,\omega_{1})\tau_{3}}{\zeta_{l}+\nu_{m}-\omega_{1}} + \frac{\tau_{3}a(p,\omega_{1})}{\zeta_{l}-\omega_{1}} \right) \right] + \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d\nu_{1}d\nu_{2}d\nu_{3}d\mu_{1}d\mu_{2}}{(2\pi)^{5}} \left[f(-\mu_{1}) + N(\nu_{3}) \right] d(k,\nu_{3}) \\
\times \frac{a(p,\nu_{1})\tau_{3}}{\zeta_{l}+\nu_{m}-\nu_{1}} \left[\frac{\mathbf{f}_{p-k}^{(1)}(\mu_{1},\mu_{2})}{\zeta_{l}-\mu_{1}-\nu_{3}} + \frac{\mathbf{f}_{p-k}^{(2)}(\mu_{1},\mu_{2})}{\zeta_{l}+\nu_{m}-\mu_{1}-\nu_{3}} \right] \frac{\tau_{3}a(p,\nu_{2})}{(\nu_{m}-\mu_{2})(\zeta_{l}-\nu_{2})} . \quad (3.8)$$

The Fermi and Planck functions are abbreviated by f and N, respectively. From Eq. (3.8) we can derive two coupled equations for $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ by calculating first the discontinuity across the real ζ_l axis at $\zeta_l = \omega$ for fixed imaginary ν_m and then the discontinuity across the real ν_m axis at $\nu_m = \nu$, or by carrying out these operations in the opposite order. The two equations are

$$\mathbf{f}_{\mathbf{p}^{(1)}}(\omega,\nu) = -(\mathbf{p}/2m)(2\omega+\nu)a(p,\omega+\nu)\tau_{3}a(p,\omega) + (2\pi)^{-8} \int d^{3}k d\nu_{1} d\nu_{2} d\nu_{3} d\mu_{1} d\mu_{2} [f(-\mu_{1})+N(\nu_{3})]d(k,\nu_{3})$$

$$\times a(p,\nu_{1})\tau_{3} \{\mathbf{f}_{\mathbf{p}-\mathbf{k}^{(1)}}(\mu_{1},\mu_{2})2 \operatorname{Im}[(\omega-\nu_{3}-\mu_{1}-i0^{+})^{-1}(\omega-\nu_{2}-i0^{+})^{-1}]$$

$$\times 2 \operatorname{Im}[(\omega+\nu-\nu_{1}-i0^{+})^{-1}(\nu-\mu_{2}-i0^{+})^{-1}] + \mathbf{f}_{\mathbf{p}-\mathbf{k}^{(2)}}(\mu_{1},\mu_{2})2\pi\delta(\omega-\nu_{2})$$

$$\times 2 \operatorname{Im}[(\nu-\mu_{2}-i0^{+})^{-1}(\omega+\nu-\nu_{1}-i0^{+})^{-1}(\omega+\nu-\nu_{3}-\mu_{1}-i0^{+})^{-1}]\}\tau_{3}a(p,\nu_{2}), \quad (3.9)$$
and
$$\mathbf{f}_{\mathbf{p}^{(1)}}(\omega,\nu) + \mathbf{f}_{\mathbf{p}^{(2)}}(\omega+\nu,\nu) = (2\pi)^{-7} \int d^{3}k d\nu_{1} d\nu_{2} d\nu_{3} d\mu_{1} [f(-\mu_{1})+N(\nu_{3})]d(k,\nu_{3})a(p,\nu_{1})\tau_{3}$$

$$\times \{\mathbf{f}_{\mathbf{p}-\mathbf{k}^{(1)}}(\mu_{1},\nu)2 \operatorname{Im}[(\omega+\nu-\nu_{1}-i0^{+})^{-1}(\omega-\nu_{3}-\mu_{1}-i0^{+})^{-1}(\omega-\nu_{2}-i0^{+})^{-1}] + \mathbf{f}_{\mathbf{p}-\mathbf{k}^{(2)}}(\mu_{1},\nu)$$

We note that the second and third terms on the right of Eqs. (3.6) and (3.8), which are discontinuity terms of the type we have previously omitted, do not in fact contribute to the double spectral functions of physical interest. Let us now consider Eq. (3.10) in the limit $\nu \to 0$. We make the Ansatz

$$\mathbf{f}_{\mathbf{p}}^{(i)}(\omega,0) = (\mathbf{p}/m)g^{(i)}(\epsilon_{p},\omega), \quad i=1,2,$$
 (3.11)

 $\times 2 \operatorname{Im} \lceil (\omega + \nu - \nu_3 - \mu_1 - i0^+)^{-1} (\omega + \nu - \nu_1 - i0^+)^{-1} (\omega - \nu_2 - i0^+)^{-1} \rceil \} \tau_3 a(\rho, \nu_2). \quad (3.10)$

and obtain from (3.10) an equation for $g^{(1)}+g^{(2)}$. On the right-hand side of this equation there occurs the angular factor $(\mathbf{p}-\mathbf{k})\cdot\mathbf{p}/p^2$, which may be replaced by 1 if one neglects terms of order k_BT/μ and k_BT/cp_F (where c is a typical velocity of sound). The d^3k integration may now be transformed into integrations over k, or the phonon

frequencies $\omega_{\lambda}(k)$, where λ designates the phonon branch, and over ϵ_{p-k} . Since the latter integral runs over practically all ϵ_{p-k} , we introduce the functions

$$g^{(i)}(\omega) = \int_{-\infty}^{\infty} d\epsilon g^{(i)}(\epsilon, \omega)$$
 (3.12)

and integrate both sides of the equation for $g^{(1)}(\epsilon,\omega)+g^{(2)}(\epsilon,\omega)$ over all ϵ . The result can be written in the form

$$g^{(1)}(\omega) + g^{(2)}(\omega) = (2\pi)^{-4} \int d\epsilon d\nu_1 d\nu_2 d\nu_3 d\mu_1 \sum_{\lambda} \int d\omega_{\lambda} F_{\lambda}(\omega_{\lambda}) d\lambda_{\lambda}(\omega_{\lambda}, \nu_3) [f(-\mu_1) + N(\nu_3)] a(\epsilon, \nu_1)$$

$$\times \tau_3 [g^{(1)}(\mu_1) + g^{(2)}(\mu_1)] \tau_3 a(\epsilon, \nu_2) 2 \operatorname{Im} [(\omega - \nu_1 - i0^+)^{-1}(\omega - \nu_3 - \mu_1 - i0^+)^{-1}(\omega - \nu_2 - i0^+)^{-1}]. \quad (3.13)$$

Above we have followed Schrieffer *et al.* in characterizing the phonons by frequency distributions $F_{\lambda}(\omega_{\lambda})$ and spectral functions $d_{\lambda}(\omega_{\lambda}, \nu)$ which are of the form

$$d_{\lambda}(\omega_{\lambda},\nu) = 2\pi\alpha_{\lambda}^{2}(\omega_{\lambda})[\delta(\nu-\omega_{\lambda})-\delta(\nu+\omega_{\lambda})], \quad (3.14)$$

where α_{λ} measures the strength of the electron-phonon coupling. All of the constants arising from transforming the variables of integration are contained in α_{λ} .

The functions $g^{(i)}(\omega)$ are matrices in the Nambu space. We make the decomposition

$$g^{(i)}(\omega) = g_0^{(i)}(\omega) 1 + g_1^{(i)}(\omega) \tau_1 + g_2^{(i)}(\omega) \tau_2 + g_3^{(i)}(\omega) \tau_3. \quad (3.15)$$

On the left side of (3.13) we are interested only in the τ_3 component because only this enters the integral for the thermal conductivity. One finds that the terms containing $g_2^{(i)}$ on the right of (3.13) do not enter the τ_3 component of the equation. The terms proportional to $g_0^{(i)}$ and $g_1^{(i)}$ make no contribution to the τ_3 component when integrated over ϵ since the integrands are odd in ϵ . We are then left with a homogeneous integral equation for $g_3^{(1)}(\omega)+g_3^{(2)}(\omega)$. We may now explicitly do the ϵ integral and perform the sum in the Nambu space. When this is done one finds that the right-hand side is zero because there occurs an integral we have met with in Sec. II, namely,

$$I_{1} = \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr} \left[\tau_{3} \mathcal{G}(\epsilon, \omega - i0^{+}) \tau_{3} \mathcal{G}(\epsilon, \omega - i0^{+}) \right] = 0. \quad (3.16)$$

(See Appendix C for the evaluation.) We have thus shown that

$$\frac{1}{2\mu} \int d\epsilon \mathbf{p} \cdot \text{Tr} \{ \tau_3 [\mathbf{f}_{\mathbf{p}}^{(1)}(\omega, 0) + \mathbf{f}_{\mathbf{p}}^{(2)}(\omega, 0)] \}
= g_3^{(1)}(\omega) + g_3^{(2)}(\omega) = 0. \quad (3.17)$$

Hereafter we shall write

$$g_3^{(1)}(\omega) = -g_3^{(2)}(\omega) \equiv g(\omega).$$
 (3.18)

One can also show, using time reversal invariance and (3.17), that in our approximation we may take $g(\omega)$ to be real (Appendix B).

Using (3.17) in the general expression for the thermal conductivity (3.5) we see that the second term in this last equation does not contribute. The third term on the right-hand side of (3.5) also does not contribute. To see this we take the derivative of both sides of Eq. (3.10) with respect to ν and then set $\nu=0$. We now remove the vector dependence by an Ansatz similar to (3.11) and integrate the resulting equation for scalar quantities over all ϵ . The procedure is identical to that described above Eq. (3.13). We then take the τ_3 projection and find that the right-hand side is zero either because of oddness in ϵ or because of (3.16) and (3.17). In other words, in our approximation we have

$$\int d\epsilon \mathbf{p} \cdot \operatorname{Tr} \left\{ \tau_{3} \frac{\partial}{\partial \nu} \left[\mathbf{f}_{\mathbf{p}}^{(1)}(\omega, \nu) + \mathbf{f}_{\mathbf{p}}^{(2)}(\omega + \nu, \nu) \right] \right|_{\nu=0} \right\} = 0.$$
(3.19)

We therefore see that the thermal conductivity (3.5) is entirely determined by the τ_3 component of $\mathbf{p} \cdot \mathbf{f}_{\mathbf{p}}^{(2)}(\omega,0)$ or equivalently, through Eqs. (3.11), (3.12), (3.15), and (3.18), by the scalar function $g(\omega)$. To determine this function let us consider Eq. (3.9) in the limit $\nu=0$. In the curly bracket on the right of (3.9) there are eight terms which arise from explicitly taking the imaginary parts. It is convenient to increase this number from eight to ten by adding and subtracting the term $4\pi^4\mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(1)}(\mu_1,\mu_2)\delta(\omega-\nu_3-\mu_1)\delta(\omega-\nu_2)\delta(\omega-\nu_1)\delta(\mu_2)$ in the curly bracket. The resulting equation for $\mathbf{f}_{\mathbf{p}}^{(1)}(\omega,0)$ may be written in the form

$$\begin{split} \mathbf{f}_{\mathbf{p}}^{(1)}(\omega, 0) &= -a(p, \omega) \tau_{3} \mathbf{\Gamma}(\mathbf{p}, \omega) \tau_{3} a(p, \omega) \\ &+ (2\pi)^{-4} \bigg\{ \int d^{3}k d\nu \big[f(\nu - \omega) + N(\nu) \big] d(k, \nu) \frac{1}{2} \big[\mathcal{G}(p, \omega - i0^{+}) \tau_{3} \mathbf{f}_{\mathbf{p} - \mathbf{k}}^{(1)}(\omega - \nu, 0) \tau_{3} \mathcal{G}(p, \omega + i0^{+}) \\ &+ \mathcal{G}(p, \omega + i0^{+}) \tau_{3} \mathbf{f}_{\mathbf{p} - \mathbf{k}}^{(1)}(\omega - \nu, 0) \tau_{3} \mathcal{G}(p, \omega - i0^{+}) \big] \bigg\} + \mathbf{f}_{\mathbf{p}}'(\omega, 0) \,. \end{split}$$
 (3.20)

(The occurrence of the +i0+'s in the arguments of the Green's functions in the curly bracket will be important in what follows.) In (3.20) $\Gamma(\mathbf{p},\omega)$ describes the corrected vertex associated with the ladder approximation and is given by

$$\Gamma(\mathbf{p},\omega) = \omega(\mathbf{p}/m)\tau_{3} - \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d\mu_{1}d\mu_{2}d\nu_{3}}{(2\pi)^{3}} \{ [f(-\mu_{1}) + N(\nu_{3})]d(k,\nu_{3}) [\mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(1)}(\mu_{1},\mu_{2}) + \mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(2)}(\mu_{1},\mu_{2})] \times \operatorname{Re}[(\omega - \nu_{3} - \mu_{1} - i0^{+})^{-1}(-\mu_{2} - i0^{+})^{-1}] \}. \quad (3.21)$$

The function $\mathbf{f}_{\mathbf{p}}'(\omega,0)$ consists of four interference terms. The explicit form is

$$\mathbf{f}_{\mathbf{p}'}(\omega,0) = 2 \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d\mu_{1}d\nu_{3}}{(2\pi)^{2}} \Big[f(-\mu_{1}) + N(\nu_{3}) \Big] d(k,\nu_{3}) P \frac{1}{\omega - \nu_{3} - \mu_{1}} \Big[\operatorname{Reg}(p,\omega - i0^{+}) \Big] \tau_{3} \Big[\mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(1)}(\mu_{1},0) + \mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(2)}(\mu_{1},0) \Big]$$

$$\times \tau_{3} \Big[\operatorname{Img}(p,\omega - i0^{+}) \Big] - 2 \int \frac{d^{3}k}{(2\pi)^{3}} \int \frac{d\mu_{2}d\nu_{3}}{(2\pi)^{2}} \Big[f(\nu_{3} - \omega) + N(\nu_{3}) \Big] d(k,\nu_{3}) P \Big(\frac{1}{\mu_{2}} \Big)$$

$$\times \{ \Big[\operatorname{Img}(p,\omega - i0^{+}) \Big] \tau_{3} \mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(1)}(\omega - \nu_{3},\mu_{2}) \tau_{3} \Big[\operatorname{Reg}(p,\omega - i0^{+}) \Big] + \Big[\operatorname{Reg}(p,\omega - i0^{+}) \Big] \tau_{3} \mathbf{f}_{\mathbf{p}-\mathbf{k}}^{(2)}(\omega - \nu_{3},\mu_{2}) \tau_{3} \Big[\operatorname{Img}(p,\omega - i0^{+}) \Big] \}. \quad (3.22)$$

We shall return in a moment to \mathbf{f}' . However, let us first consider the vertex corrections (3.21). In general, we may define the Fourier coefficients of a vertex operator by the relation

$$\chi(\mathbf{p}, \zeta_{1} + \nu_{m}; \mathbf{p}, \zeta_{1})
= (\mathbf{p}/2m) [g(p, \zeta_{1} + \nu_{m})\tau_{3} + \tau_{3}g(p, \zeta_{1})]
- g(p, \zeta_{1} + \nu_{m}) \mathbf{\Gamma}_{\mathbf{p}}(\zeta_{1} + \nu_{m}, \zeta_{1})g(p, \zeta_{1}).$$
(3.23)

The function $\Gamma(\mathbf{p},\omega)$ is then related to the analytic continuation of the Fourier series coefficients by

$$\Gamma(p,\omega) = \Gamma_{p}(\omega + \nu, \nu)|_{\nu=0}, \qquad (3.24)$$

where

$$\Gamma_{p}(\omega+\nu,\nu) = \frac{1}{2} \{ \Gamma_{p}(\zeta_{l}+\nu_{m},\zeta_{l}) \Big|_{\substack{\zeta_{l}=\omega-i0^{+}\\\nu_{m}=\nu-i0^{+}\\\nu_{m}=\nu+i0^{+}}} + \Gamma_{p}(\zeta_{l}+\nu_{m},\zeta_{l}) \Big|_{\substack{\zeta_{l}=\omega+i0^{+}\\\nu_{m}=\nu+i0^{+}}}. \quad (3.25)$$

It is straightforward to verify that $\Gamma(\mathbf{p},\omega)$ as defined by (3.23)–(3.25) is in fact given by (3.21) in the ladder approximation of (3.6).

There exists a Ward identity, reflecting the conservation of energy density, for the vertex function introduced above. This Ward identity has been discussed with great clarity by Langer,⁸ and it is therefore not necessary to give the derivation here. The result in terms of Fourier series coefficients is¹⁶

$$\Gamma_{\mathbf{p}}(\zeta_{l},\zeta_{l}) = -\zeta_{l}\nabla_{\mathbf{p}}G^{-1}(p,\zeta_{l})
= -\zeta_{l}\nabla_{\mathbf{p}}[\zeta_{l} - ((p^{2}/2m) - \mu)\tau_{3} - \Sigma(p,\zeta_{l})]. (3.26)$$

We notice that in the Eliashberg approximation of neglecting the momentum dependence of the self-energy operator the vertex correction is zero. We may therefore make the replacement

$$\Gamma(\mathbf{p},\omega) \to (\mathbf{p}/m)\omega\tau_3.$$
 (3.27)

In a more exact treatment one would have to include the effective mass and wave function renormalization corrections implied by (3.26).

We now return to Eq. (3.20), remove the vector dependence, and integrate both sides of the resulting equation over all ϵ . The τ_3 component of this equation is then found to be

$$g(\omega) = -\frac{\pi\omega}{|\operatorname{Im}Z(\omega^{2} - \Delta^{2})^{1/2}|} \left(1 + \frac{\omega^{2} - |\Delta|^{2}}{|\omega^{2} - \Delta^{2}|} \right)$$

$$\times \left\{ 1 - \frac{1}{2\omega} \int \frac{d\nu}{2\pi} \sum_{\lambda} \int d\omega_{\lambda} F_{\lambda}(\omega_{\lambda}) d_{\lambda}(\omega_{\lambda}, \nu) \right.$$

$$\times \left[f(\nu - \omega) + N(\nu) \right] g(\omega - \nu) \right\} + g'(\omega), \quad (3.28)$$

where $g'(\omega)$ comes from the interference terms \mathbf{f}' given in (3.22). Whereas in the other terms of (3.20) the τ_3 component on the left is only coupled to the τ_3 component on the right, g' turns out to depend only on g_2 . The

Eliashberg approximation to neglect such terms. It should also be remarked that since the Ward identity (3.26) follows from the strict conservation of energy density it requires the inclusion in the vertex function of the heat current \mathbf{u}_{ph} introduced above Eq. (2.2) and then rapidly discarded. This means that in using (3.26) we are including a part of the "phonon-drag" thermal conduction. Since we have already argued that processes of this type have a negligible effect on the thermal conductivity, their inclusion here is of no consequence.

¹⁶ In Langer's result (Ref. 8) there occur additional terms due to the nonlocality in space of the Coulomb interaction he considers. Such terms do not occur for the electron-phonon interaction. For the direct Coulomb interaction it is in any case consistent with the

explicit form we find is

$$g'(\omega) = \frac{i\pi\omega \operatorname{Im}\Delta}{|\operatorname{Im}Z(\omega^{2} - \Delta^{2})^{1/2}||\omega^{2} - \Delta^{2}|} \times \left\{ \int \frac{d\nu d\mu_{1}}{(2\pi)^{2}} \left[f(-\mu_{1}) + N(\nu) \right] \right.$$

$$\times \sum_{\lambda} \int d\omega_{\lambda} \frac{F_{\lambda}(\omega_{\lambda}) d_{\lambda}(\omega_{\lambda}, \nu)}{(\omega - \nu - \mu_{1})_{p}} \left[g_{2}^{(1)}(\mu_{1}) + g_{2}^{(2)}(\mu_{2}) \right] \right.$$

$$+ \int \frac{d\nu d\mu_{2}}{(2\pi)^{2}} \left[f(\nu - \omega) + N(\nu) \right]$$

$$\times \sum_{\lambda} \int d\omega_{\lambda} \frac{F_{\lambda}(\omega_{\lambda}) d_{\lambda}(\omega_{\lambda}, \nu)}{(\mu_{2})_{p}} \times \left[g_{2}^{(1)}(\omega - \nu, \mu_{2}) - g_{2}^{(2)}(\omega - \nu, \mu_{2}) \right] \right\}. \quad (3.29)$$

The coupling between the τ_3 and the τ_2 components, though physically interesting, appears to be of negligible importance for our problem. In the first place, an examination of Eq. (3.13) shows that the τ_2 component on the left is coupled only to the τ_2 component on the right. In other words, $g_2^{(1)}(\omega) + g_2^{(2)}(\omega)$ satisfies a linear homogeneous integral equation. Therefore this quantity can at most be nonzero for certain values of the electronphonon coupling constant, an unphysical possibility which it seems safe to ignore. In comparing the remaining term in Eq. (3.29) with the homogeneous term in (3.28) we encounter the ratio $[Im\Delta(\omega)/\omega]$. From the numerical results of Schrieffer et al. we see that for the frequencies of interest, i.e., $\omega < 10kT_c$, this factor is less than 0.1 at T=0 and consequently exceedingly small just below $T = T_c$. Thus, barring the occurrence of other large factors, the second term in (3.29) is also negligible. An order of magnitude comparison of the integrands of this term and the homogeneous term in (3.28) yields the ratio $\Gamma(\omega-\nu)/(\omega-\nu)$, where $\Gamma(\omega-\nu)$ is a typical width at frequency $(\omega - \nu)$. Although this factor is not small over the entire region of interest, it is never large. It therefore seems safe to conclude that the terms in g' are of no significance. These terms evidently describe weakrelaxation processes peculiar to the superconducting state which involve the motion of condensed pairs relative to the single-particle excitations.¹⁷ We plan to study these processes further.

Since the coupling between different components in the Nambu space came solely from g' in (3.28), none remains when this term is omitted. On introducing the spectral function (3.14) we then obtain

$$g(\omega) = \frac{\pi\omega}{|\operatorname{Im} Z(\omega^{2} - \Delta^{2})^{1/2}|} \left(1 + \frac{\omega^{2} - |\Delta|^{2}}{|\omega^{2} - \Delta^{2}|} \right)$$

$$\times \left\{ 1 - (2\omega)^{-1} f^{-1} (-\omega) \sum_{\lambda} \int d\omega_{\lambda} \alpha_{\lambda}^{2} (\omega_{\lambda}) F_{\lambda}(\omega_{\lambda}) \right.$$

$$\times \left[f(\omega_{\lambda} - \omega) (1 + N(\omega_{\lambda})) g(\omega - \omega_{\lambda}) + f(-\omega_{\lambda} - \omega) N(\omega_{\lambda}) g(\omega + \omega_{\lambda}) \right] \right\}. \quad (3.30)$$

It follows from (3.30) that $g(\omega)$ is odd in ω , which one also expects on general grounds. Further one sees that near T=0 $g(\omega)=0$ for $\omega<\Delta_0$. From (3.5) and our subsequent analysis we see that the thermal conductivity K is determined once $g(\omega)$ is known by the quadrature

$$K = -\frac{n}{4mk_B T^2} \int_0^\infty \frac{d\omega}{2\pi} \operatorname{sech}^2(\frac{1}{2}\beta\omega) g(\omega). \quad (3.31)$$

The Hartree-Fock result (2.17) is recovered if we approximate $g(\omega)$ by the inhomogeneous term of (3.30). In the small width limit $|\operatorname{Im}[Z(\omega^2-\Delta^2)^{1/2}]|^{-1} \to (\omega^2-\Delta_1^2)^{1/2}/\omega\Gamma$. If one introduces instead of $g(\omega)$ a new function $G(\omega)$ defined according to

$$g(\omega) = -\pi \operatorname{sgn}\omega(\omega^2 - \Delta_1^2)^{1/2} \left(1 + \frac{\omega^2 - \Delta_1^2}{|\omega^2 - \Delta_1^2|}\right) G(\omega), (3.32)$$

one obtains an integral equation for $G(\omega)$ which is identical to the integral equation obtained previously from the Boltzmann equation. [Essentially Eq. (2.18) of I if the differences in phonon spectra used are taken into account.]

If the width is not small, (3.30) is the most convenient form for numerical calculations. The complex functions $\Delta(\omega)$ and $Z(\omega)$ have to be determined from the set of integral equations given in Appendix A.

IV. CONCLUSIONS

In spite of some anfractuous analysis, we have been led to a relatively straightforward scheme for calculating the electronic thermal conductivity of strongly coupled superconductors. The Eliashberg approximation of weak momentum dependence is essential for much of the final simplicity. We have found in this approximation that the thermal conductivity is determined by an integral of the expression $\omega \operatorname{sech}^2(\frac{1}{2}\beta\omega)g(\omega)$ over all excitation energies ω . The function $g(\omega)$ plays the role of the deviation from an equlibrium distribution and satisfies the generalized Boltzmann equation (3.30).

If one neglects the difference between the transport and the scattering cross sections, or equivalently keeps only the inhomogeneous term of the integral equation (3.30), one recovers the result of the Hartree-Fock

¹⁷ This is a situation reminiscent of the collective excitation which occurs in the response of the superconductor to finite frequency and wave number electromagnetic disturbances.

approximation of Sec. II. In this case, for frequencies not too far above the gap edge $g(\omega)$ becomes approximately equal to $-2\pi(\omega^2-\Delta_1^2)^{1/2}/\Gamma(\omega)$, where $\Gamma(\omega)$ plays the role of a width parameter and is in the weak-coupling limit identical with the reciprocal of twice the quasiparticle lifetime as calculated in II. The expression for $\Gamma(\omega)$ is $\Gamma(\omega) \approx |Z_2(\omega^2-\Delta_1^2)-Z_1\Delta_1\Delta_2|\omega^{-1}$. The renormalization function $Z(\omega)$ and the gap function $\Delta(\omega)$ have to be determined from the Eliashberg gap equations given in Appendix A.

The gap equations have been solved for lead by Schrieffer et al. in the limit of zero temperature, but not for temperatures near T_c which are of interest here. We can therefore only speculate about the manner in which the great reduction in the thermal conductivity of superconducting lead might be explained by our theory. The calculations in I have shown that in the small width limit the decrease of K_s/K_n with decreasing temperature is mainly due to the increase of Δ_1 in the factor $(\omega^2 - \Delta_1^2)^{1/2}$ in the integrand of K_s , while $T^3\Gamma_s^{-1}$ (as a function of $\beta\omega$) is relatively insensitive to changes in temperature near T_c . Let us assume that this is also true for lead. Then it is important to note that near T_c energies up to about $\omega_m = 10k_BT_c$ contribute to the heat current. This means that the first peak in the curve for $\Delta_1(\omega)$ calculated by Schrieffer et al. which occurs at $\omega_1^t = 4.4 \times 10^{-3} \text{ eV} \approx 10 k_B T_c \text{ occurs roughly at } \omega_m. \text{ If}$ the shape of the $\Delta_1(\omega)$ curve were preserved at temperatures near T_c or, more precisely, if the ratio $\Delta_1(\omega)/\Delta_0$ were nearly independent of T, then the effective gap Δ_1 for the excitations predominantly carrying the heat current would clearly be much greater than the gap edge Δ_0 . This would lead to a substantial reduction of K_s/K_n compared to the value obtained in the small width limit.

To go beyond the Hartree-Fock approximation one must numerically solve the integral equation (3.30). From the experience of the calculations reported in I, it is not expected that this more exact treatment will drastically affect the thermal conductivity. Nevertheless, without a solution of the integral equation it seems difficult to estimate the errors introduced by the Hartree-Fock approximation. It is worth noting that the most complicated part of the integral equation (3.30), which depends on the solution of the gap equations, is the Hartree-Fock value of $g(\omega)$ which occurs as a factor in both the homogeneous and inhomogeneous terms. It should also be noted that the same electronphonon coupling strengths, α_{λ} , and phonon frequency distributions $F_{\lambda}(\omega_{\lambda})$ occur in the integral equation for $g(\omega)$ and those for $\Delta(\omega)$ and $Z(\omega)$.

In the small width limit, i.e., $\alpha_{\lambda} \rightarrow 0$, we have indicated how (3.30) may be transformed into the Bloch-Boltzmann equation for the superconducting state. A byproduct of the analysis given in the present paper has thus been the justification of the use of this equation, as in I, for example. In our extreme long-wavelength low-frequency limit the only validity criterion for the use of the Boltzmann equation is that well defined quasi-

particles exist in the thermally excited frequency range below roughly $10k_BT$. This criterion also applies to the normal state, and when it fails one must resort to the more general approach described in this paper.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor L. P. Kadanoff for a useful discussion. Much of the contribution of the first named author (V. A.) was performed during a six week visit to the Bell Telephone Laboratories during the summer of 1963. The authors are happy to take the opportunity to thank the Bell Telephone Laboratories and in particular their friends and colleagues in the Theoretical Physics Department for their gracious hospitality.

APPENDIX A

In the Nambu representation the superconductive approximation to the electronic self-energy operator has the Fourier coefficients

$$\Sigma(p,\zeta_l) = -\frac{1}{\beta} \sum_{\nu_m} \int \frac{d^3q}{(2\pi)^3} \tau_3 \times \Im(p-q,\zeta_l-\nu_m) \tau_3 D(q,\nu_m). \quad (A1)$$

Here

$$\mathcal{G}^{-1}(\mathbf{p},\mathbf{z}) = \mathbf{z} - \epsilon_{\mathbf{p}} - \Sigma(\mathbf{p},\mathbf{z}) \tag{A2}$$

and the Nambu Ansatz for $\Sigma(p,z)$ is

$$\Sigma(p,z) = z\zeta_p(z) + \chi_p(z)\tau_3 + \phi_p(z)\tau_1. \tag{A3}$$

Following Eliashberg we neglect χ the even in frequency component of the diagonal (in Nambu space) part of Σ as contributing only a shift in the chemical potential. Then \mathfrak{G}^{-1} has the form given in Eq. (2.12), namely

$$S^{-1}(p,z) = zZ(z) - \epsilon \tau_3 - \phi(z)\tau_1,$$
 (A4)

where $Z(z)=1-\zeta(z)$. The functions ϕ and Z have the properties

$$Z(z^*) = Z^*(z); \quad Z(-z) = Z(z),$$

 $\phi(z^*) = \phi^*(z); \quad \phi(-z) = \phi(z).$ (A5)

Z(z) is even because $z\zeta(z)$ is the odd component of the diagonal part of Σ . The function $\phi(z)$ may be taken to be even in z for s state pairing because of spin-rotation invariance, time-reversal symmetry, and spatial-inversion symmetry. Using (A5) it is easily seen that the spectral function $a(p,\omega)$ defined by Eq. (2.13) has the properties

$$\operatorname{Tr}[a(p,\omega)] = \operatorname{Tr}[a(p,-\omega)],$$

$$\operatorname{Tr}[\tau_i a(p,\omega)] = -\operatorname{Tr}[\tau_i a(p,-\omega)].$$
(A6)

Now we insert the spectral representations for \mathfrak{g} and D

¹⁸ Questions of symmetry are very carefully considered in P. Nozieres, *Theory of Interacting Fermion Systems* (W. A. Benjamin, Inc., New York, 1963).

[Eqs. (2.10) and (3.7)] into (A1) and perform the sum over ν_m . We then make the weak-momentum approximation for ϕ and Z and perform the integral over d^3q in the manner discussed in Sec. III. The integral of $a(\epsilon,\omega)$ over all ϵ which is needed here is given by 6,10

$$\int_{-\infty}^{\infty} d\epsilon a(\epsilon, \omega) = -2\pi \operatorname{Re} \left\{ \frac{\omega Z(\omega) + \phi(\omega) \tau_1}{\epsilon_1(\omega)} \right\}, \quad (A7)$$

where ϵ_1 is the root of $\epsilon^2 + \phi^2(\omega) - (\omega - i0^+)^2 Z^2(\omega) = 0$ which lies in the upper half-plane. [For real argument ω , $\phi(\omega)$ and $Z(\omega)$ are given by (2.16). After performing the steps outlined above, we decompose the integral equation for $\Sigma(z)$ in the Nambu space and equate coefficients of 1 and τ_3 on the right and left sides. The symmetries (A6) may be used to simplify the equations. The final equations are

$$\Delta(z) = \frac{1}{Z(z)} \int_{0}^{\infty} d\omega_{1} \operatorname{Re} \left\{ \frac{\Delta(\omega_{1})}{\left[\omega_{1}^{2} - \Delta^{2}(\omega_{1})\right]^{1/2}} \right\} \sum_{\lambda} \int d\omega_{\lambda} \alpha_{\lambda}^{2}(\omega_{\lambda}) F_{\lambda}(\omega_{\lambda})$$

$$\times \left\{ \left[N(\omega_{\lambda}) + f(-\omega_{1}) \right] \left[(\omega_{1} + \omega_{\lambda} + z)^{-1} + (\omega_{1} + \omega_{\lambda} - z)^{-1} \right] \right.$$

$$\left. - \left[N(\omega_{\lambda}) + f(\omega_{1}) \right] \left[(-\omega_{1} + \omega_{\lambda} + z)^{-1} + (-\omega_{1} + \omega_{\lambda} - z)^{-1} \right] \right\},$$

$$z \left[1 - Z(z) \right] = \int_{0}^{\infty} d\omega_{1} \operatorname{Re} \left\{ \frac{\omega_{1}}{\left[\omega_{1}^{2} - \Delta^{2}(\omega_{1}) \right]^{1/2}} \right\} \sum_{\lambda} \int d\omega_{\lambda} \alpha_{\lambda}^{2}(\omega_{\lambda}) F_{\lambda}(\omega_{\lambda})$$

$$\times \left\{ \left[N(\omega_{\lambda}) + f(-\omega_{1}) \right] \left[(\omega_{1} + \omega_{\lambda} + z)^{-1} - (\omega_{1} + \omega_{\lambda} - z)^{-1} \right] \right\},$$

$$+ \left[N(\omega_{\lambda}) + f(\omega_{1}) \right] \left[(-\omega_{1} + \omega_{\lambda} + z)^{-1} - (-\omega_{1} + \omega_{\lambda} - z)^{-1} \right] \right\}.$$

$$(A8)$$

The physical values of Δ and Z are obtained by setting $z=\omega-i0^+$ in (A8). The sign of the square root in (A8) is to be determined by $\operatorname{Im}\{Z(\omega^2-\Delta^2)^{1/2}\}<0$.

APPENDIX B

The spectral representation (3.4) for the object $\chi_{ij}(t_1,t_2,t_3) \equiv T \langle \psi_i(t_1) \mathbf{u}(t_2) \psi_j^{\dagger}(t_3) \rangle$ follows from its periodicity properties for imaginary times. (We suppress the spatial arguments for brevity.) Consider the region of time Ret₁, t_2 , $t_3=0$; $0>\text{Im}t_1$, t_2 , $t_3>-\beta\equiv i\tau$, and let Torder the operators from right to left in order of increasing negative imaginary time.⁷ Then measuring energies with respect to the chemical potential, and using the cyclic invariance of the trace operation contained in the ground canonical ensemble average, one finds the periodicity properties

$$\mathfrak{X}_{ij}(0,t_2,t_3) = -\mathfrak{X}_{ij}(\tau,t_2,t_3) ,
\mathfrak{X}_{ij}(t_1,0,t_3) = +\mathfrak{X}_{ij}(t_1,\tau,t_3) ,
\mathfrak{X}_{ij}(t_1,t_2,0) = -\mathfrak{X}_{ij}(t_1,t_2,\tau) .$$
(B1)

As a result we may make the Fourier series expansion

$$\chi_{ij}(t_1, t_2, t_3) = \frac{1}{\tau^3} \sum_{lmn} \chi_{ij}(n, m, l) e^{-i\zeta_n t_1} e^{-i\nu_m t_2} e^{-i\zeta_l t_3}, \quad (B2)$$

where $\zeta_n = (2n+1)\pi/\tau$, $\nu_m = 2\pi m/\tau$, $\zeta_l = (2l+1)\pi/\tau$. Because $\chi(t_1,t_2,t_3) = \chi(t_1-t_2,t_2-t_3)$ we expect $\chi(nml)$ to be zero unless $\zeta_n + \nu_m + \zeta_l = 0$. Inverting the Fourier series

$$\chi_{ij}(n,m,l) = \int_{0}^{\tau} dt_{1} \int_{0}^{\tau} dt_{2} \int_{0}^{\tau} dt_{3} \chi_{ij}(t_{1},t_{2},t_{3}) \times e^{i\zeta_{1}t_{2}} e^{i\gamma_{m}t_{2}} e^{i\zeta_{1}t_{3}}.$$
(B3)

To do the integral we break up the domain of integration into six regions corresponding to the six time-ordered constituents of χ . In each of these regions the time dependence of the Heisenberg operators can be displayed and the integrals trivially performed. One verifies that $\chi(nml)$ is indeed zero unless the condition written above (B3) is satisfied. It is convenient to take as independent variables ζ_l and ν_m and to introduce $\chi(\zeta_l + \nu_m, \zeta_l) \equiv \tau \chi(l+m, -m, -l-1)$ so that the Fourier expansion reads

$$\chi_{ij}(t_1 - t_2, t_2 - t_3) = \frac{1}{\tau^2} \sum_{lm} \chi_{ij}(\zeta_l + \nu_m, \zeta_l) \\
\times e^{-i(\zeta_l + \nu_m)(t_1 - t_2)} e^{-i\zeta_l(t_2 - t_3)}.$$
(B4)

After explicitly carrying out the time integrals in (B3) in the manner indicated above, one finds that the Fourier coefficient $\chi(\zeta_l + \nu_m, \zeta_l)$ can be written in the form (3.4). The spectral functions $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ obtained explicitly in this way are sums of products of three matrix elements, and two delta functions involving the frequencies ω_1 and ω_2 . After some rearrangement one finds that the spectral functions may be written compactly in the form

$$\mathbf{f}_{ij}^{(1)}(\omega_{1},\omega_{2}) = \int_{-\infty}^{\infty} dt_{1} \int_{-\infty}^{\infty} dt_{2}$$

$$\times \langle \{ [\mathbf{u}(-t_{2}), \psi_{i}(0)], \psi_{j}^{\dagger}(-t_{1}) \} \rangle$$

$$\times e^{i\omega_{1}t_{1}} e^{i\omega_{2}t_{2}}, \quad (B5)$$

and
$$\mathbf{f}_{ij}^{(2)}(\omega_{1},\omega_{2}) = \int_{-\infty}^{\infty} dt_{1} \int_{-\infty}^{\infty} dt_{2} \langle \{ [\mathbf{u}(-t_{2}), \psi_{j}^{\dagger}(0)], \psi_{i}(t_{1}) \} \rangle \times e^{i\omega_{1}t_{1}} e^{i\omega_{2}t_{2}}. \quad (B6)$$

Above, the curly bracket indicates the anticommutator and the square bracket the commutator.

We now wish to substantiate the remarks made after Eq. (3.18) about the reality of $g(\omega)$. If one uses time reversal invariance on the closed forms (B5) and (B6) one finds the relation

$$\mathbf{f}_{ij}^{(1)}(\omega_1,\omega_2) = -(\tau_2)_{ik}\mathbf{f}_{lk}^{(2)}(-\omega_1,\omega_2)^*(\tau_2)_{lj}. \quad (B7)$$

Further from explicit complex conjugation of (B5) and (B6) one finds

$$\mathbf{f}_{ii}^{(1)}(\omega_1,\omega_2)^* = -\mathbf{f}_{ii}^{(2)}(\omega_1,-\omega_2).$$
 (B8)

From (B7) and (B8) we can derive the exact identity

$$\operatorname{Tr}[\mathbf{f}^{(2)}(\omega_1,\omega_2)\tau_3] = -\operatorname{Tr}[f^{(1)}(\omega_1,-\omega_2)\tau_3]^*. \quad (B9)$$

In the ladder approximation we have proved that

$$\int d\epsilon \mathbf{p} \cdot \text{Tr} \{ \tau_3 [\mathbf{f}^{(1)}(\omega, 0) + \mathbf{f}^{(2)}(\omega, 0)] \} = 0. \quad (B10)$$

It follows from (B9) and (B10) that in our approximation

$$\int d\epsilon \mathbf{p} \cdot \mathrm{Tr} [\tau_{3} \mathbf{f}^{(1)}(\omega, 0)]$$

$$= \int \left\{ d\epsilon \mathbf{p} \cdot \mathrm{Tr} [\tau_{3} \mathbf{f}^{(1)}(\omega, 0)] \right\}^{*}. \quad (B11)$$

Using the definition of $g(\omega)$ contained in Eqs. (3.18), (3.15), and (3.11) we see that (B11) implies that this function is real.

APPENDIX C

Here we sketch the evaluation of the integrals I_1 and I_2 given in Eqs. (2.14) and (2.15). Although the evaluation is straightforward it seems worth presenting, particularly because (2.14) plays an important role in Sec. III.

Consider first I_1 . We have using (2.12)

$$I_{1} = \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr} \left[\tau_{3} \mathcal{G}(\epsilon, \omega - i0^{+}) \tau_{3} \mathcal{G}(\epsilon, \omega - i0^{+}) \right]$$

$$= 2 \int_{-\infty}^{\infty} d\epsilon \frac{\omega^{2} Z^{2} + \epsilon^{2} - \phi^{2}}{(\epsilon - \epsilon_{1})^{2} (\epsilon + \epsilon_{1})^{2}}, \qquad (C1)$$

where $\epsilon = \pm \epsilon_1$ are the roots of

$$\omega^2 Z^2 - \epsilon^2 - \phi^2 = 0. \tag{C2}$$

We choose $+\epsilon_1$ to lie in the upper half-plane. Then by contour integration

$$I_1 = 4\pi i \left[-\frac{\omega^2 Z^2 - \phi^2}{4\epsilon_1^3} + \frac{1}{4\epsilon_1} \right] = 0,$$
 (C3)

where the last step follows from (C2). The integral I_2 , on the other hand, is given by

$$I_{2} = \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr} \left[\tau_{3} \Im(\epsilon, \omega - i0^{+}) \tau_{3} \Im(\epsilon, \omega + i0^{+}) \right]$$

$$= 2 \int_{-\infty}^{\infty} d\epsilon \frac{\omega^{2} |Z|^{2} + \epsilon^{2} - |\phi|^{2}}{(\epsilon - \epsilon_{1})(\epsilon + \epsilon_{1})(\epsilon - \epsilon_{1}^{*})(\epsilon + \epsilon_{1}^{*})}.$$
(C4)

Since ϵ_1 is in the upper half-plane, so is $-\epsilon_1^*$. By a straightforward contour integration,

$$I_{2} = 4\pi i \left[\frac{\omega^{2}|Z|^{2} - |\phi|^{2} + \epsilon_{1}^{2}}{8i\epsilon_{1} \operatorname{Im}\epsilon_{1} \operatorname{Re}\epsilon_{1}} + \frac{\omega^{2}|Z|^{2} - |\phi|^{2} + (\epsilon_{1}^{*})^{2}}{8i \operatorname{Re}\epsilon_{1} \operatorname{Im}\epsilon_{1} \cdot \epsilon_{1}^{*}} \right]$$

$$= \frac{\pi}{\operatorname{Im}\epsilon_{1}} \left[\frac{\omega^{2}|Z|^{2} - |\phi|^{2} + |\epsilon_{1}|^{2}}{|\epsilon_{1}|^{2}} \right]. \tag{C5}$$

Using (C2) and the relation $\Delta(\omega) = \phi(\omega)/Z(\omega)$, (C5) may be put in the form given in (2.15).