Thermal Transport Coefficients of a Superconductor*

J. M. LUTTINGER
Columbia University, New York, New York
(Received 20 July 1964)

The phenomenological equations of a superconductor in the presence of temperature gradients are discussed. From these, an expression for the thermal conductivity as a correlation function of the Kubo type is given.

I. INTRODUCTION

RECENTLY there has been a considerable amount of theoretical work done on the thermal conductivity of superconductors,[1] based on the modern theory of superconductivity. While for some substances (Sn, In, for example) quite good agreement is obtained with experiment, for others (Hg,Pb) the agreement is rather poor. We shall not discuss in this paper the origin of such difficulties, which could lie in the insufficiency of the model or the technique used for the computation. Rather, we shall be concerned with the more general question of how to obtain a rigorous expression for the thermal conductivity of a superconductor, once the model is given. The kind of expression we have in mind is the correlation function type (such as the Kubo formula for the electrical conductivity), which enables one to calculate the desired coefficient rigorously in principle, though it may be very difficult in practice. Such a formula can then be used as a starting point for a discussion of a specific model.

Now the difficulty in obtaining such an expression for a superconductor is essentially the following. In ordinary metals the thermal conductivity is expressed in terms of the phenomenological coefficients relating the current flow and energy flow to the driving forces, i.e., the electric field, density and temperature gradients. These equations may be written (taking an isotropic substance for simplicity) in the form[2]

$$\mathbf{j}=L_1\left[\mathbf{E}-\frac{T}{e}\nabla\left(\frac{\mu}{T}\right)\right]+L_2\left(-\frac{1}{T}\nabla T\right), \quad (1.1)$$

$$\mathbf{j}^E=L_3\left[\mathbf{E}-\frac{T}{e}\nabla\left(\frac{\mu}{T}\right)\right]+L_4\left(-\frac{1}{T}\nabla T\right), \quad (1.2)$$

where $\mathbf{j}$, $\mathbf{j}^E$ are the electric current and energy current densities, respectively, $\mathbf{E}$ the electric field, e the electronic charge, μ the chemical potential and T the temperature. The coefficients L_i are the phenomenological transport coefficients. The thermal conductivity κ is defined as the ratio of the energy current density to the negative temperature gradient, under the condition that no electric current flows. Using (1.1) and (1.2) this definition gives at once

$$\kappa=(1/T)(L_4-L_2L_3/L_1). \quad (1.3)$$

This definition cannot directly be taken over for a superconductor, since for a superconductor one knows that the electrical conductivity (and therefore L_1) becomes infinite. Indeed, one would expect all the L_1 to become infinite, since an accelerating superfluid, although not expected to carry entropy, would be expected to carry charge and energy. Therefore, the expression (1.3) no longer makes sense for a superconductor. Nonetheless, it is known experimentally that a superconductor does have a finite thermal conductivity, and the question arises as to what takes the place of (1.3). For this purpose the phenomenological equations (1.1) and (1.2) for a normal conductor must be replaced by some others. The program of this paper is to suggest certain phenomenological equations, based partly on the idea of the two-fluid model and partly on experiment. In terms of the coefficients which enter into these equations we obtain an expression for the thermal conductivity. Finally, we show how to express this in terms of a correlation function expression of the Kubo type.

II. THE PHENOMENOLOGICAL EQUATIONS

In formulating the phenomenological equations necessary for describing thermal effects in superconductors, we shall assume that the basic concepts of the two-fluid pictures are valid.[3] That is, we shall assume that the macroscopic state of the superconductor may be described by giving charge densities for super and normal fluids (ρ_s and ρ_n) and local velocities ($\mathbf{v}_s$ and $\mathbf{v}_n$) for them. Then the total charge density and current density are

$$\rho=\rho_n+\rho_s, \quad (2.1)$$

$$\mathbf{j}=\rho_n\mathbf{v}_n+\rho_s\mathbf{v}_s\equiv\mathbf{j}_n+\mathbf{j}_n. \quad (2.2)$$

It is assumed that the ratio of the normal and superfluid densities is given by the equilibrium function of

* Supported in part by the U. S. Office of Naval Research.

[1] J. Bardeen, G. Rickhazen, and L. Terwordt, Phys. Rev. **113**, 982 (1959); B. T. Geilikman, Zh. Eksperim. i Teor. Fiz. **34**, 1042 (1958) [English transl.: Soviet Phys.—JETP **7**, 721 (1958)]; L. Kadanoff and P. Martin, Phys. Rev. **124**, 670 (1961); L. Tewordt, *ibid.* **129**, 657 (1963); V. Ambegaokar and L. Tewordt, *ibid.* **134**, A805 (1964).

[2] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), Chap. VIII.

[3] F. London, *Superfluids* (John Wiley & Sons Inc., New York, 1954), Vol. 2.

the local temperature, i.e., equilibrium between normal and superfluid sets in much more rapidly than any process we consider. The fundamental assumption of the two-fluid theory is that the normal component behaves very much like electrons in a normal metal, while the super-fluid part is freely accelerated by any forces acting on it. We shall make this statement more precise below.

Let us first consider how the presence of an homogeneous electric field affects the superfluid. Clearly,

$$\partial \mathbf{v}_s/\partial t=(e/m)\mathbf{E}\,, \qquad \partial \mathbf{j}_s/\partial t=(e\rho_s^0/m)\mathbf{E}\,, \tag{2.3}$$

where we are working in the linear approximation, ρ_s^0 being the equilibrium charge density of superfluid, m the mass of the electron. This is the usual acceleration equation in the London theory. If, however, the system is not homogeneous, i.e., if the temperature or density vary from point to point, another term must be added to the right-hand side of (2.3). We assert that (2.3) becomes

$$\partial \mathbf{j}_s/\partial t=(e\rho_s^0/m)(\mathbf{E}-(1/e)\boldsymbol{\nabla}\mu)\,. \tag{2.4}$$

The extra $\boldsymbol{\nabla}\mu$ term is well-known in the theory of superfluid He, having first been introduced by Landau[4] and justified under rather general conditions by Khalatnikov.[5] Roughly speaking, (2.4) asserts that the electrochemical potential $\mu+e\varphi$ (φ being the electrostatic potential) which is constant in equilibrium acts as the potential energy function for the superfluid. While it is possible to obtain (2.4) from a simplified model,[6] I do not know of any general proof. I shall simply assume (2.4), later on giving what I believe to be a very strong experimental indication of its validity.

We next consider the equations for the normal fluid. The most direct way of obtaining them is to consider the entropy production in the usual manner of the theory of irreversible processes.[7] That is, we assume that the total entropy S of the system may be written in the form

$$S=\int d\mathbf{r}s(u_i,n)\,, \tag{2.5}$$

where u_i and n are the internal energy and number density of the system at the point $\mathbf{r}$, respectively, s is the entropy per unit volume (the same function of u_i and n as in equilibrium), and the integration extends over the entire system. Differentiating (2.5) with respect to time we obtain

$$\frac{\partial S}{\partial t}=\int d\mathbf{r}\left\{\left(\frac{\partial s}{\partial u_i}\right)_n\frac{\partial u_i}{\partial t}+\left(\frac{\partial s}{\partial n}\right)_{u_i}\frac{\partial n}{\partial t}\right\} =\int d\mathbf{r}\left\{\frac{1}{T}\frac{\partial u_i}{\partial t}-\frac{\mu}{T}\frac{\partial n}{\partial t}\right\}, \tag{2.6}$$

using standard thermodynamic identities. By means of conservation of particle number and energy we may write

$$\partial n/\partial t+(1/e)\boldsymbol{\nabla}\cdot\mathbf{j}=0\,, \tag{2.7}$$

$$\partial u/\partial t+\nabla\cdot\mathbf{j}^E=\mathbf{E}\cdot\mathbf{j}\,. \tag{2.8}$$

In (2.8), u is the total energy of the system per unit volume and $\mathbf{j}^E$ is the energy-current density. Equation (2.8) simply expresses the fact that the rate at which energy increases in a fixed volume is equal to the rate at which electrical work is done on the particles in the volume, minus the rate at which energy flows across the surface. The internal energy is the energy minus the kinetic energies of the normal and superfluid.

$$u_i=u-\frac{m}{2}\left(\frac{\rho_s}{e}\right)v_s^2-\frac{m}{2}\left(\frac{\rho_n}{e}\right)v_n^2\,. \tag{2.9}$$

Therefore,

$$\frac{\partial u_i}{\partial t}=\frac{\partial u}{\partial t}-\frac{m\rho_s^0}{e}\mathbf{v}_s\cdot\frac{\partial \mathbf{v}_s}{\partial t}-\frac{m\rho_n^0}{e}\mathbf{v}_n\cdot\frac{\partial \mathbf{v}_n}{\partial t}\,, \tag{2.10}$$

neglecting terms of higher than second order in the velocity or currents. The last term of (2.10) may be neglected in comparison with the second, since the normal current is negligibly accelerated by quasistatic driving forces, while the supercurrent is freely accelerated. Thus,

$$\begin{aligned}\frac{\partial u_i}{\partial t}&=\frac{\partial u}{\partial t}-\rho_s^0\mathbf{v}_s\cdot\left(\mathbf{E}-\frac{1}{e}\boldsymbol{\nabla}\mu\right)\\ &=\partial u/\partial t-\mathbf{j}_s\cdot(\mathbf{E}-(1/e)\boldsymbol{\nabla}\mu)\\ &=\mathbf{E}\cdot\mathbf{j}-\mathbf{j}_s\cdot(\mathbf{E}-(1/e)\boldsymbol{\nabla}\mu)-\boldsymbol{\nabla}\cdot\mathbf{j}^E\,,\end{aligned} \tag{2.11}$$

using (2.8). Substituting (2.11) and (2.7) in (2.6) we obtain

$$\begin{aligned}\frac{\partial S}{\partial t}&=\int d\mathbf{r}\left\{\frac{\mu}{T}\frac{1}{e}\boldsymbol{\nabla}\cdot\mathbf{j}+\frac{1}{T}\left[\left(\mathbf{E}-\frac{1}{e}\boldsymbol{\nabla}\mu\right)\cdot\mathbf{j}_n+\frac{1}{e}\boldsymbol{\nabla}\mu\cdot\mathbf{j}-\boldsymbol{\nabla}\cdot\mathbf{j}^E\right]\right\}\\ &=\int d\mathbf{r}\left\{\frac{1}{T}\left(\mathbf{E}-\frac{1}{e}\boldsymbol{\nabla}\mu\right)\cdot\mathbf{j}_n+\boldsymbol{\nabla}\left(\frac{1}{T}\right)\cdot\left(\mathbf{j}^E-\frac{\mu}{e}\mathbf{j}\right)-\boldsymbol{\nabla}\cdot\frac{1}{T}\left(\mathbf{j}^E-\frac{\mu}{e}\mathbf{j}\right)\right\}.\end{aligned} \tag{2.12}$$

---

[4] L. Landau, Zh. Eksperim. i Teor. Fiz. **5**, 71 (1941).

[5] I. M. Khalatnikov, Fortschr. Physik **5**, 287 (1957).

[6] It is not difficult to show (2.4) in the framework of the Gor'kov formulation of the BCS theory. I am grateful to Dr. P. Anderson of the Bell Telephone Laboratories for pointing this out to me.

[7] For example, S. R. de Groot and P. Mazur, *Non-Equilibrium Thermo-dynamics* (North-Holland Publishing Company, Amsterdam, 1962).

It is clear from (2.12) that we may regard

$$\mathbf{J}_s \equiv (1/T)(\mathbf{j}^E - (\mu/e)\mathbf{j}) \tag{2.13}$$

as the entropy current density, and that the irreversible production of entropy per unit volume ($\dot{\sigma}$) is given by

$$\dot{\sigma} = \frac{1}{T}\left[\left(\mathbf{E} - \frac{1}{e}\nabla\mu\right)\cdot\mathbf{j}_n + \mathbf{X}_T\cdot\left(\mathbf{j}^E - \frac{\mu}{e}\mathbf{j}\right)\right], \tag{2.14}$$

where

$$\mathbf{X}_T \equiv -(1/T)\nabla T. \tag{2.15}$$

We notice that in (2.14) the supercurrents do not contribute to the entropy production. This is a consequence of the assumption (2.4). Just as in the case of the He II, this conforms to our notion that the superfluid flow is a reversible phenomenon producing no entropy.

Since we would expect the normal current and entropy flow to be of the same form as in a normal conductor, (2.14) suggests that we write (continuing to assume for simplicity an isotropic system)

$$\mathbf{j}_n = K_1(\mathbf{E} - (1/e)\nabla\mu) + K_2\mathbf{X}_T, \tag{2.16}$$
$$\mathbf{j}^E - (\mu/e)\mathbf{j} = K_3(\mathbf{E} - (1/e)\nabla\mu) + K_4\mathbf{X}_T,$$

as the remaining phenomenological equations of the system. The K_i are new phenomenological coefficients, taking the place of the old L_i for a normal metal. Finiteness of the K_i insures that the entropy production is finite, and positive definiteness of the matrix of the coefficients K_i insures that it is positive. Further, from the Onsager relationships we must have

$$K_2 = K_3 \tag{2.17}$$

in the absence of a magnetic field.[8]

If the system is in a stationary state then by (2.4) we must have

$$\mathbf{E} = (1/e)\nabla\mu. \tag{2.18}$$

From (2.16) we obtain

$$\mathbf{j}_n = K_2\mathbf{X}_T, \tag{2.19}$$

$$\mathbf{j}^E - (\mu/e)\mathbf{j} = K_4\mathbf{X}_T. \tag{2.20}$$

The amount of superfluid flow $\mathbf{j}_s$ must be determined by the boundary conditions. For example, in the thermal conductivity problem, the ends of the sample are insulated so that $\mathbf{j}=0$. Therefore $\mathbf{j}_n$ is given by (2.19) and $\mathbf{j}_s$ by

$$\mathbf{j}_s = -\mathbf{j}_n. \tag{2.21}$$

[8] In these equations, of course, all quantities must vary with space and time more slowly than any characteristic length or time in the system. Therefore, if magnetic fields are present the penetration depth must be much greater than the coherence length, or we must deal with samples much thinner than the penetration depth. To find the distribution of currents and magnetic fields, one actually must supplement our equations with Maxwell's equations and the second London equation. We shall mainly be interested in thermal flow problems where the total electric current is zero and therefore no magnetic field is generated.

Under these conditions we therefore have

$$\mathbf{j}^E = K_4\mathbf{X}_T = (1/T)K_4(-\nabla T) \tag{2.22}$$

and the thermal conductivity of a superconductor is given by

$$\kappa = (1/T)K_4. \tag{2.23}$$

This replaces (1.3) appropriate to a normal conductor.

In a certain sense (2.23) may be obtained from (1.3). If we consider not stationary phenomena but fields and temperature gradients varying as $e^{i\omega t}$, then (2.4) becomes

$$i\omega\mathbf{j}_s = (e\rho_s^0/m)(\mathbf{E} - (1/e)\nabla\mu). \tag{2.24}$$

Using (2.24) and (2.16), one may easily verify that

$$\begin{aligned}\mathbf{j} &= \left(\frac{e\rho_s^0}{mi\omega} + K_1\right)\left[\mathbf{E} - \frac{T}{e}\nabla\left(\frac{\mu}{T}\right)\right] + \left[\frac{\mu}{e}\left(\frac{e\rho_s^0}{mi\omega}\right) + K_2 + \frac{\mu}{e}K_1\right]\mathbf{X}_T,\\ \mathbf{j}^E &= \left[\frac{\mu}{e}\left(\frac{e\rho_s^0}{mi\omega}\right) + K_3 + \frac{\mu}{e}K_1\right]\left[\mathbf{E} - \frac{T}{e}\nabla\left(\frac{\mu}{T}\right)\right]\\ &\quad + \left[K_4 + \frac{\mu}{e}(K_2+K_3) + \left(\frac{\mu}{e}\right)^2 K_1 + \left(\frac{\mu}{e}\right)^2\left(\frac{e\rho_s^0}{mi\omega}\right)\right]\mathbf{X}_T.\end{aligned} \tag{2.25}$$

These equations take the place of (1.1) and (1.2) when the system goes superconducting. We may think of the usually regular coefficients L_i as all acquiring an extra term proportional to $1/\omega$, i.e., as becoming infinite in the same way as the frequency goes to zero. If we apply (1.3) to these new coefficients and then let $1/\omega$ go to zero, we find just (2.23).

There are some other interesting consequences of our phenomenological equations. From (2.18) it follows that there is no thermoelectric effect in superconductors. In a normal metal we have, under the condition of no current flow

$$\mathbf{E} = \frac{1}{e}\nabla\mu + \frac{L_1(\mu/e) - L_2}{L_1}\mathbf{X}_T. \tag{2.26}$$

If we make a loop out of normal and superconducting materials, and integrate $\mathbf{E}$ around this loop we get, using (2.26) and (2.18),

$$\begin{aligned}\text{e.m.f.} &= \oint \mathbf{E}\cdot d\mathbf{l} = \oint d\mathbf{l}\cdot\nabla\left(\frac{\mu}{e}\right) + \int_{\substack{\text{in normal}\\ \text{metal}}} d\mathbf{l}\cdot\mathbf{X}_T\frac{L_1(\mu/e) - L_2}{L_1}\\ &= \int_{\substack{\text{in normal}\\ \text{metal}}} d\mathbf{l}\cdot\mathbf{X}_T\frac{L_1(\mu/e) - L_2}{L_1}.\end{aligned} \tag{2.27}$$

That is, only the normal metal contributes to the thermal e.m.f. This result has been known for a very long time, and has been established with great accuracy.[9] It is perhaps the most convincing experimental proof of the validity of (2.4).

Another interesting conclusion from (2.18) is the following. Since charge neutrality is very accurately maintained in a metal because of the large electrostatic forces, a temperature gradient will produce a negligible density gradient. Therefore, (2.18) becomes

$$e(\varphi_1-\varphi_2)=\mu(T_1,n_0)-\mu(T_2,n_0), \qquad (2.28)$$

where φ_1 and φ_2 are the potentials at the ends of a piece of superconductor and T_1 and T_2 the corresponding temperatures. Thus a temperature difference will engender a potential difference across the metal. This is the analog for superconductors of the fountain effect in He II. If we estimate $\varphi_1-\varphi_2$ by assuming the temperature dependence of μ is roughly like that of a normal conductor (which it must be at temperatures not far from the transition temperature) and take a temperature difference of a few degrees at a temperature of a few degrees, we obtain

$$e(\varphi_1-\varphi_2)/\mu\sim 10^{-7}-10^{-8}. \qquad (2.29)$$

Since μ is of the order of volts this means a potential difference of a tenth to a hundreth of a microvolt. Though small, this should be measureable if not masked by other effects. Such a measurement would provide us with a direct measurement of the thermodynamic functions of the electrons in the superconducting state. It should be mentioned that an effect of the same order of magnitude exists for normal metals but it involves the transport coefficients L_1 and L_2 as well as the equilibrium thermodynamic functions.

III. FORMAL EXPRESSION FOR THE THERMAL CONDUCTIVITY

In order to obtain a formal expression for the thermal conductivity we must see how K_4 is expressed as a correlation function. To do this we may proceed as we did[10] in obtaining the thermal transport coefficients of normal metals or simple fluids. In I we introduced an extra field ψ which coupled with the energy density. In the phenomenological equations, extra driving terms proportional to $\nabla\psi$ were added in such a way as to insure that in equilibrium no currents flow. We have, using I (A30) and (A31), that in equilibrium

$$T_0\nabla(\mu/T)=e\mathbf{E}, \qquad (3.1)$$

$$T_0\nabla(1/T)=\nabla\psi. \qquad (3.2)$$

These are equivalent to

$$\mathbf{E}-(1/e)\nabla\mu-(\mu_0/e)\nabla\psi=0, \qquad (3.3)$$

$$\mathbf{X}_T-\nabla\psi=0. \qquad (3.4)$$

Clearly the phenomenological equations in the presence of ψ become

$$\frac{\partial\mathbf{j}_s}{\partial t}=\frac{e\rho_s^0}{m}\left(\mathbf{E}-\frac{1}{e}\nabla\mu-\frac{\mu_0}{e}\nabla\psi\right), \qquad (3.5)$$

$$\mathbf{j}_n=K_1\left(\mathbf{E}-\frac{1}{e}\nabla\mu-\frac{\mu_0}{e}\nabla\psi\right)+K_2(\mathbf{X}_T-\nabla\psi), \qquad (3.6)$$

$$\mathbf{j}^E-\frac{\mu}{e}\mathbf{j}=K_3\left(\mathbf{E}-\frac{1}{e}\nabla\mu-\frac{\mu_0}{e}\nabla\psi\right)+K_4(\mathbf{X}_T-\Delta\psi), \qquad (3.7)$$

since this insures that the driving forces for the currents vanish in equilibrium.

Just as in I, we consider these equations in the "rapid" limit, i.e., $\mathbf{q}$ (the propagation vector of the disturbance) goes to zero before s (the rate at which the fields are turned on). Using (3.5), (3.6), (3.7) in conjunction with the equation of continuity for charge and energy densities, we see that, as before, in this limit $\nabla\mu$ and ∇T vanish. Therefore for the $\mathbf{q}$th Fourier component and (say) the x spatial component we have

$$\left(j_x^E-\frac{\mu_0}{e}j_x\right)_{\mathbf{q}}=-iq_x\left[K_3\varphi_{\mathbf{q}}+\left(K_4+\frac{\mu_0}{e}K_3\right)\psi_{\mathbf{q}}\right]V. \qquad (3.8)$$

On the other hand, we have from I (2.22),

$$j_{\mathbf{q}x}=-iq_x[L_{xx}^{(1)}\varphi_{\mathbf{q}}+\tilde{L}_{xx}^{(2)}\psi_{\mathbf{q}}]V, \qquad (3.9)$$

$$j_{\mathbf{q}x}^E=-iq_x[L_{xx}^{(3)}\varphi_{\mathbf{q}}+\tilde{L}_{xx}^{(4)}\psi_{\mathbf{q}}]V, \qquad (3.10)$$

where the L's are given by I (2.23) in terms of correlation functions. Combining (3.9) and (3.10), and comparing with (3.8) we obtain

$$K_3=L_{xx}^{(3)}-(\mu_0/e)L_{xx}^{(1)},$$

$$K_4+(\mu_0/e)K_3=\tilde{L}_{xx}^{(4)}-(\mu_0/e)\tilde{L}_{xx}^{(2)},$$

or

$$K_4=\tilde{L}_{xx}^{(4)}-(\mu_0/e)(\tilde{L}_{xx}^{(2)}+L_{xx}^{(3)})+(\mu_0/e)L_{xx}^{(1)}. \qquad (3.11)$$

Finally, using I (2.23) the thermal conductivity becomes[11]

$$\kappa=\frac{1}{T}K_4=\frac{1}{TV}\lim_{s\to 0}\int_0^\infty dte^{-st}\times\int_0^\beta d\beta'\left\langle\left(j_x^E-\frac{\mu_0}{e}j_x\right)_0\left(j_x^E-\frac{\mu_0}{e}j_x\right)_0\right\rangle_0. \qquad (3.12)$$

[9] See, for example, D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1962), p. 86 ff.

[10] J. M. Luttinger, Phys. Rev. **135**, A1505 (1964). We shall refer to this paper as I.

[11] Just as in I, if one takes explicit account of the long-range Coulomb forces, one must proceed to the $q=0$ limit with a little caution, though no real difficulty is encountered.

The expression (3.12) gives the *exact* answer for the thermal conductivity of a superconductor, but it has been used already[1] as an extremely accurate approximate expression. The somewhat crude justification for this is that if one takes (1.3) for a *normal* metal it is easy to see that it only differs from (3.12) by an amount of relative order of magnitude $(kT/\mu)^2$, which is completely negligible at the temperatures of importance for superconductivity. Since (3.12) makes sense in the superconductor (i.e., remains finite) and is extremely accurate for the normal metal, it was natural to assume it valid to a high degree of approximation for a superconductor.

ACKNOWLEDGMENTS

I would like to thank the Brookhaven National Laboratory for its hospitality during the summer of 1964, when this work was completed.

PHYSICAL REVIEW VOLUME 136, NUMBER 6A 14 DECEMBER 1964

Free-Energy Difference Between Normal and Superconducting States

JOHN BARDEEN* AND MICHAEL STEPHEN
Department of Physics, Yale University, New Haven, Connecticut
(Received 27 July 1964)

The Eliashberg expression for the free-energy difference between superconducting and normal states for an electron-phonon interaction model is evaluated so as to estimate the errors involved in expressions based on the weak-coupling limit. It is shown that the major correction comes from the difference in self-energy terms Σ_{1s} and Σ_{1n} and is relatively of order $[(\Delta/\omega_0)\ln(\Delta/\omega_0)]^2$, where ω_0 is an average phonon energy. The correction may be appreciable for strong-coupling superconductors such as lead.

ONE of the present authors[1] with Cooper and Schrieffer derived an expression for the free-energy difference between normal and superconducting states, $\Omega_s-\Omega_n$, based on a model subject to the following approximations:

(1) The Fermi surface is isotropic.

(2) The gap parameter Δ is independent of energy over the important range of integration, a few times Δ.

(3) The self-energy Σ_1 is the same in normal and superconducting states, and is also independent of energy over the relevant range. One may then include Σ_1 in the renormalized quasiparticle energies.

With these assumptions, $\Omega_s-\Omega_n$ may be expressed as a function of Δ and T. The specific interactions which give rise to superconductivity enter only through Δ. Thus one may use the expression to derive an empirical $\Delta(T)$ from experimental measurements of the free energy difference, as obtained for example from the critical field.[2]

The latter two assumptions are presumably valid in the weak-coupling limit, $\Delta\ll\omega_0$, where ω_0 is an average phonon energy. The purpose of the present paper is to derive more general formulas for the free-energy difference between normal and superconducting states and thus to estimate the errors involved in the Bardeen-Cooper-Schrieffer (BCS) expression. The calculations are based on a theory of Eliashberg[3] which includes electron-phonon interactions in a general way but omits effects of Coulomb interactions, except as they may be included in the renormalization of the quasiparticle energies. The major corrections arise from differences in Σ_1 between normal and superconducting states arising from the phonon interaction.

The general expression derived by Eliashberg[4] for the free energy per unit volume of the superconducting state is

$$\begin{aligned}\Omega_s=&-(2/V\beta)\sum_P[\tfrac{1}{2}\ln(-\varphi(P))\\&+\Sigma_1(P)G(P)-\Sigma_2(P)F(-P)]\\&+(1/2V\beta)\sum_q[\ln(-D^{-1}(q))+\pi(q)D(q)]\\&+(1/V^2\beta^2)\sum_{PP'}\alpha_{p-p'}{}^2[G(P)D(P-P')G(P')\\&-F(P)D(P-P')F(-P')],\end{aligned}\quad(1)$$

where

$$P=(\mathbf{p},\zeta_l),\quad q=(\mathbf{q},\nu_l),\quad \zeta_l=(2l+1)\pi i/\beta,\quad \nu_l=2l\pi i/\beta;$$

$$G(P)=(-\zeta_l-\epsilon_p+\Sigma_1(-P))/\varphi(P);\quad(2)$$

$$F(P)=-\Sigma_2(-P)/\varphi(P);\quad(3)$$

$$\varphi(P)=[\zeta_l-\epsilon_p+\Sigma_1(P)]\times[\zeta_l+\epsilon_p-\Sigma_1(-P)]-|\Sigma_2(P)|^2;$$

$$D^{-1}(q)=D_0^{-1}(q)-\pi(q),\quad D_0(q)=2\omega_q{}^{0\,2}/(\omega_q{}^{0\,2}-\nu_l{}^2).\quad(4)$$

---

* On leave from the University of Illinois, Urbana, Illinois, February–June, 1964.

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

[2] D. K. Finnemore, D. E. Mapother, and R. W. Shaw, Phys. Rev. **118**, 127 (1960).

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

[4] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **43**, 1005 (1962) [English transl.: Soviet Phys.—JETP **16**, 780 (1963)].