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.

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Free-Energy Difference Between Normal and Superconducting States

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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

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

where

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

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

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

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

$$D^{-1}(q)=D_0{}^{-1}(q)-\pi(q),\quad D_0(q)=2\omega_q{}^{02}/(\omega_q{}^{02}-\nu_l{}^2).\quad(4)$$

* 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)].

The energies ϵ_p are measured from the Fermi energy μ, $\omega_q{}^0$ is the unrenormalized phonon energy, and $\alpha_{p-p'}$ is the coupling constant entering the electron-phonon interaction. We assume everywhere that ϵ_p is small compared to μ so that there is symmetry between electrons and holes. Then μ will be independent of temperature and the same in normal and superconducting states.

The expression (1) for Ω_s is analogous to a similar expression given by Luttinger and Ward[5] for the free energy of an interacting electron system. It has the useful feature that it is stationary with respect to variations in Σ_1, Σ_2, and π if these quantities are given by

$$\Sigma_{1s}(P)=(1/V\beta)\sum_{P'}\alpha_{p-p'}{}^2G(P')D(P-P'), \tag{5}$$

$$\Sigma_{2s}(P)=(1/V\beta)\sum_{P'}\alpha_{p-p'}{}^2F(P')D(P-P'), \tag{6}$$

$$\pi_s(q)=-(2\alpha_q{}^2/V\beta)\times\sum_P[G(P+q)G(P)-F(P+q)F(-P)]. \tag{7}$$

The corresponding expression for Ω_n, the free energy in the normal state, is similar to (1) except that now $\Sigma_2=F=0$ and Σ_{1n} and π_n differ by small amounts from their values Σ_{1s} and π_s in the superconducting state. The free energy difference $\Omega_s-\Omega_n$ may be calculated by making use of the fact that Ω_n is stationary with respect to variations in Σ_1 and π. If in the expression for Ω_n we replace Σ_{1n} by Σ_{1s} and π_n by π_s and call the result Ω_{ns}, then Ω_{ns} will differ from Ω_n by terms quadratic in the differences $(\Sigma_{1s}-\Sigma_{1n})$ and $(\pi_s-\pi_n)$. The magnitude of these errors is estimated below and shown to be negligibly small.

The expression for $\Omega_s-\Omega_{ns}$ can be simplified by use of (5) and (6). We find

$$\Omega_s-\Omega_{ns}=-(1/V\beta)\times\sum_P[\ln(\varphi_s(P)/\varphi_{ns}(P))-\Sigma_2(P)F(-P)]+C, \tag{8}$$

where C is given by

$$C=-(1/V^2\beta^2)\sum_{PP'}\alpha_{p-p'}{}^2[G(P)-G_{ns}(P)]\times D(P-P')[G(P')-G_{ns}(P')] \tag{9}$$

and is a small correction in the weak-coupling limit. Here G_{ns} is the electron Green's function for the normal metal except that Σ_{1n} is replaced by Σ_{1s}. Similarly φ_{ns} is obtained from φ_s by setting $\Sigma_2=0$.

The momentum dependence of Σ_1 and Σ_2 is unimportant and following Nambu[6] we define

$$\zeta Z(\zeta)=\zeta+\Sigma_1(\zeta),\quad \Delta(\zeta)=\Sigma_2(\zeta)/Z(\zeta). \tag{10}$$

[5] J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1418 (1960).
[6] Y. Nambu, Phys. Rev. **117**, 648 (1960).

The integration over momenta in (8) can then be carried out, and we find:

$$\Omega_s-\Omega_{ns}=[2\pi N(0)/\beta]\sum_l\{(-\zeta_l{}^2)^{1/2}-(\Delta^2(\zeta_l)-\zeta_l{}^2)^{1/2}+\tfrac{1}{2}\Delta^2(\zeta_l)/[\Delta^2(\zeta_l)-\zeta_l{}^2]^{1/2}\}Z_s(\zeta_l)+C, \tag{11}$$

where $N(0)$ is the density of states of one spin at the Fermi surface.

One may evaluate C in a similar way by integrating first over momenta coordinates. It should be noted that if Σ_1 depends only on the energy variable, the sum

$$(1/\beta V)\sum_{P'}\alpha_{p-p'}{}^2G_{ns}(P')D(P-P')$$

is independent of the values of Σ_1 used in G_{ns} and is thus equal to Σ_{1n}. Thus we find

$$C=[\pi N(0)/\beta]\sum_l(Z_s-Z_n)\{(\Delta^2-\zeta_l{}^2)^{1/2}-(-\zeta_l{}^2)^{1/2}-\Delta^2/(\Delta^2-\zeta_l{}^2)^{1/2}\}. \tag{12}$$

Inserting this result in (11), we find

$$\Omega_s-\Omega_{ns}=[\pi N(0)/\beta]\sum_l\{(Z_s+Z_n)\times[(-\zeta_l{}^2)^{1/2}-(\Delta^2-\zeta_l{}^2)^{1/2}+\Delta^2/2(\Delta^2-\zeta_l{}^2)^{1/2}]+(Z_n-Z_s)\Delta^2/2(\Delta^2-\zeta_l{}^2)^{1/2}\}. \tag{13}$$

In the zero temperature limit one may replace the sum by an integral along the imaginary ω axis. By use of the summation methods of Luttinger and Ward[5] and others, one may express (13) at an arbitrary temperature as an integral along the real axis:

$$\Omega_s-\Omega_{ns}=\mathrm{Re}N(0)\int_0^\infty\left\{[Z_s(\omega)+Z_n(\omega)]\times\left(-\omega+(\omega^2-\Delta^2)^{1/2}+\frac{\Delta^2}{2(\omega^2-\Delta^2)^{1/2}}\right)+\frac{[Z_n(\omega)-Z_s(\omega)]\Delta^2}{2(\omega^2-\Delta^2)^{1/2}}\right\}\tanh\frac{\beta\omega}{2}d\omega. \tag{14}$$

Here Re means the real part.

Values of $Z(\omega)$ and $\Delta(\omega)$ have been determined for lead by Schrieffer *et al.*[7] and by Scalapino *et al.*[8] Equation (14) gives a rapidly convergent expression for calculating the free-energy difference and thus $H_c{}^2/8\pi$. It can be shown to be equivalent to an expression derived by Wada[9] by a different method. Wada's less

[7] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).
[8] D. J. Scalapino, Y. Wada, and J. Swihart, Bull. Am. Phys. Soc. **9**, 267 (1964).
[9] Y. Wada, Phys. Rev. **135**, A1481 (1964).

rapidly convergent expression is

$$\Omega_s-\Omega_n=-\mathrm{Re}N(0)\int_0^\infty\left\{[1+Z_n(\omega)]\omega-Z_s(\omega^2-\Delta^2)^{1/2}-\frac{\omega^2}{(\omega^2-\Delta^2)^{1/2}}\right\}\tanh\frac{\beta\omega}{2}d\omega. \quad (15)$$

The difference between (14) and (15) vanishes if it can be shown that

$$\mathrm{Re}N(0)\int_0^\infty\left\{\omega[Z_s(\omega)-1]-\frac{\omega^2[Z_n(\omega)-1]}{(\omega^2-\Delta^2)^{1/2}}\right\}\times\tanh\frac{\beta\omega}{2}d\omega=0, \quad (16)$$

which follows from a momentum integration of

$$\sum_P G_n(P)\Sigma_{1s}(P)=\sum_P G_s(P)\Sigma_{1n}(P). \quad (17)$$

Both sides of this equation are equal to

$$(1/\beta V)\sum_{P,P'}\alpha_{p-p'}{}^2G_n(P)G_s(P')D(P-P')$$

if it is assumed that $\pi_n=\pi_s$.

We are particularly interested here in estimating errors involved in use of the weak-coupling approximation. If Z and Δ are constants over the important range of integration, Z may be included as renormalization of the quasiparticle energies ϵ_p. This neglects small terms of order $T^4\ln T$ which come from the temperature dependence of Z (Ref. 4). The first line of (14) then reduces to the original expression of BCS, given in Eq. (3.37) of that paper. After a change of variables of integration, Eq. (14) reduces to (3.37) plus a correction C_1:

$$\Omega_s-\Omega_{ns}=-\tfrac{1}{2}N(0)\Delta^2-2N(0)\times\int_0^\infty\left\{\frac{2\epsilon^2+\Delta^2}{E}f(E)-2\epsilon f(\epsilon)\right\}d\epsilon+C_1, \quad (18)$$

where f is the Fermi function and $E=(\epsilon^2+\Delta^2)^{1/2}$. Here C_1 is given by the second line of (14):

$$C_1=\mathrm{Re}N(0)\int_0^\infty\frac{[Z_n(\omega)-Z_s(\omega)]\Delta^2}{2(\omega^2-\Delta^2)^{1/2}}\tanh\frac{\beta\omega}{2}d\omega. \quad (19)$$

For simplicity in estimating the magnitude of C_1, we make the following approximation: The coupling constant $\alpha_q{}^2$ is replaced by a constant $g=\lambda_0/N(0)$, where λ_0 is a dimensionless constant of order unity. The phonon spectrum is assumed to be of the Einstein type containing a single frequency ω_0. Then the phonon Green's function is independent of momenta, Δ and Z are regarded as constants, and Z is absorbed into the definition of the single-particle energies ϵ_p. With these approximations we find at zero temperature

$$Z_{1s}-Z_{1n}\approx\lambda_0(\Delta/\omega_0)^2\ln(\omega_0/\Delta) \qquad \omega<\omega_0$$
$$\approx\lambda_0(\Delta\omega_0/\omega^2)^2\ln(\omega_0/\Delta) \quad \omega>\omega_0, \quad (20)$$

which gives

$$C_1/(\Omega_s-\Omega_n)\approx\lambda_0[(\Delta/\omega_0)\ln(\omega_0/\Delta)]^2. \quad (21)$$

In the weak-coupling case this term is negligible, but cannot be neglected when the coupling is strong. Thus for lead $\Delta/\omega_0\approx\frac{1}{3}$ and C_1 may give a correction of more than 10%.

We turn now to a discussion of the approximations made. No error is introduced by replacing Σ_{1n} by Σ_{1s} in the calculation of Ω_n, provided that Σ_1 depends only on the energy variable and is independent of momentum, an excellent approximation. By integrating first over the momentum variable, we find

$$\Omega_n-\Omega_{ns}=-(1/\beta V)\sum_P\{\ln\varphi_n(P)/\varphi_{ns}(P)+\Sigma_{1n}(p)G_n(P)-(2\Sigma_{1s}-\Sigma_{1n})G_{ns}\}=0. \quad (22)$$

Here φ_n and G_n are the correct normal-state functions and φ_{ns} and G_{ns} the function with Σ_{1n} replaced by Σ_{1s}.

The error introduced by replacing π_n by π_s is to second order:

$$\Delta\Omega=(1/4\beta V)\sum_q[\delta D(q)/\delta\pi(q)][\pi_n(q)-\pi_s(q)]^2. \quad (23)$$

To estimate the magnitude of $\pi_n(q)-\pi_s(q)$ we use the simplifying assumptions made above. The difference depends in an unimportant way on momentum and energy and is roughly

$$\pi_s-\pi_n\approx(\lambda_0/8)(\Delta^2/\mu^2)\ln(2\omega_0/\Delta). \quad (24)$$

Since Δ/μ is of order 10^{-3}, (24) leads to a change in velocity of sound of the order of one part in 10^6. The correction (23) is completely negligible.

Thus the major correction to the BCS expression comes from C_1, and is dependent on the difference in the renormalization factors, Z_n-Z_s, between normal and superconducting states. For weak coupling, corresponding to $\Delta<\omega_0/10$, the correction is small, and the expression may be used to estimate empirically the temperature dependence of Δ from critical field or thermodynamic data. However, errors are appreciable for strong-coupling superconductors such as lead. A rapidly convergent integral is given for calculating $\Omega_s-\Omega_n$ from $Z(\omega)$ and $\Delta(\omega)$ when the coupling is strong.