Superfluidity, Flux Quantization

It follows from (22a) and invariance of J and H under (12) that there are equilibrium states for which $n(=2\nu)$ is even and nonzero in (23) and where

$$J(r) = -\int C(r,r')\left[A(r') + \frac{nch}{4\pi er'}\right] dv' \,. \quad (27)$$

Putting $A = 0$ in (23), we see that the system possesses metastable current-carrying states. Their stability may be seen to depend on the quantization of n in much the same manner as the stability of states, cited in footnote 7, depended on the discreteness of G.

For $A \neq 0$, Eq. (27) is the current–field relation for cases where the system is disturbed from a metastable state by a magnetic field. It implies the existence of trapped fluxoid[12]

$$F = nch/2e \,. \quad (28)$$

So far, we have established (27) and (28) only for even n. This restriction arises only from our method of using the transformation (12) to generate fields for which $n = 2\nu$ from those with $n = 0$. In fact, one may deduce (27) and (28) directly from (23), which we derived earlier without involving (12). In that earlier derivation[13] of (23) there is no restriction of n to even numbers. Therefore, since there appears no *a priori* reason why we should impose such a restriction, i.e., why states with n odd cannot be prepared, we shall assume the validity of (23), (27), and (28) for all integral n. In this case, the quantum of flux is seen to be $hc/2e$, as observed experimentally.[14]

[12] F. London, Ref. 5, p. 150.

[13] That derivation is general, and independent of the condition that $\bar{x} = \bar{x}_0$ at $A = 0$. The latter condition refers to a special set of fields.

[14] B. S. Deaver, Jr. and W. M. Fairbank, Phys. Rev. Letters **7**, 43 (1961).

Spatial Dependence of Pair Correlation Functions in Nonhomogeneous Superconductors*

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It has been shown by Gor'kov[1] that the theory of superconductivity can be derived in terms of differential equations relating the single-particle Green's functions $G(x,x') = -iT\langle\psi(x)\psi^\dagger(x')\rangle$ and the pair amplitude $F(x,x') = T\langle\psi(x)\psi(x')\rangle$. As the pairing is implicit in this formalism, the method is useful when treating problems in which it is not convenient to work with the explicit single-particle states. In this paper we develop a form of the theory appropriate to the investigation of superconducting contacts.

The Gor'kov equations, Fourier transformed in the relative time coordinate and written without spin indices, are[1,2]

$$\begin{aligned}(\omega - h_1)G(\mathbf{r},\mathbf{r}',\omega) &= G_0^{-1}(\mathbf{r},\bar{\mathbf{r}},\omega)G(\bar{\mathbf{r}},\mathbf{r}',\omega)\\ &= \delta^3(\mathbf{r}-\mathbf{r}') + i\Delta(\mathbf{r})F^*(\mathbf{r},\mathbf{r}',\omega)\,, \quad (1)\end{aligned}$$

$$\begin{aligned}(-\omega - h_1)F^*(\mathbf{r},\mathbf{r}',\omega) &= G_0^{-1}(\bar{\mathbf{r}},\mathbf{r},-\omega)F^*(\bar{\mathbf{r}},\mathbf{r}',\omega)\\ &= i\Delta^*(\mathbf{r})G(\mathbf{r},\mathbf{r}',\omega)\,, \quad (2)\end{aligned}$$

where h_1 is the one-particle Hamiltonian, G_0 is the Green's function in the absence of two-body interactions, a bar over a quantity signifies integration over all space, and

$$\begin{aligned}\Delta(\mathbf{r}) &\equiv V(\mathbf{r})F(\mathbf{r},\mathbf{r},t=0)\\ &= (2\pi)^{-1}V(\mathbf{r})\int_{-\infty}^{\infty} F(\mathbf{r},\mathbf{r},\omega)d\omega\,. \quad (3)\end{aligned}$$

Equations (1) and (2) can be expanded in powers of Δ as follows:

Letting

$$f(\mathbf{r},\mathbf{r}',\omega) \equiv f^{(1)}(\mathbf{r},\mathbf{r}',\omega) \equiv G_0(\mathbf{r},\bar{\mathbf{r}},\omega)i\Delta(\bar{\mathbf{r}})G_0(\mathbf{r}',\bar{\mathbf{r}},-\omega)\,, \quad (4)$$

$$f^{(n)}(\mathbf{r},\mathbf{r}',\omega) \equiv f^{(n-1)}(\mathbf{r},\bar{\mathbf{r}},\omega)i\Delta^*(\bar{\mathbf{r}})f(\bar{\mathbf{r}},\mathbf{r}',\omega)\,, \quad (5)$$

we then have

$$F(\mathbf{r},\mathbf{r}',\omega) = \sum_{n=1}^{\infty} f^{(n)}(\mathbf{r},\mathbf{r}',\omega)\,. \quad (6)$$

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[1] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].

[2] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961); V. Ambegaokar and L. P. Kadanoff, in *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962), p. 66.

For example, $f^{(2)}(\mathbf{r},\mathbf{r}',\omega)$ can be represented in the graphic fashion shown in Fig. 1(a). An electron of energy ω undergoes two-particle scattering at $\mathbf{r}_1$ into the $(N+2)$-particle ground state, creating a hole of energy $-\omega$ which undergoes scattering at $\mathbf{r}_2$, and so forth. The vertices $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ are integrated over the volume of the superconductor.

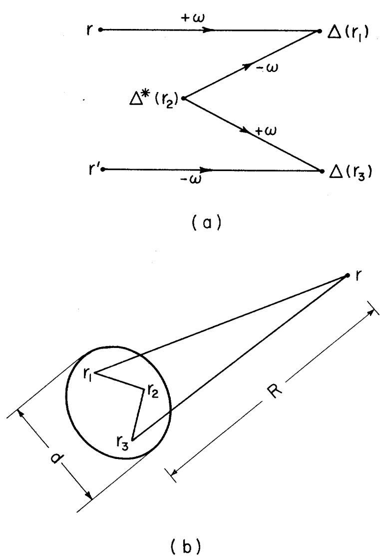

FIG. 1. Graphical representation of $f^{(2)}(\mathbf{r},\mathbf{r}',\omega)$. (a) In an infinite superconductor; (b) In a finite superconductor.

Convergence is easily established when we deal with sufficiently small superconductors. Consider a superconductor of volume Ω contained in a normal metal in which $V = 0$. Assuming that $|\Delta(\mathbf{r})| \leqslant \Delta_\infty$, the energy gap in a bulk superconductor, we obtain from (4) and (5)

$$|f(\mathbf{r},\mathbf{r}',\omega)| \leqslant \Delta_\infty \left(\frac{2m}{4\pi}\right)^2 \int_\Omega \frac{d^3\mathbf{r}''}{|\mathbf{r}-\mathbf{r}''|\cdot|\mathbf{r}'-\mathbf{r}''|} < 0.05(2m)^2\Omega^{\frac{1}{3}}\Delta_\infty\,, \quad (7)$$

$$|f^{(n)}(\mathbf{r},\mathbf{r}',\omega)| < 0.05(2m)^2\Omega^{\frac{1}{3}}\Delta_\infty[0.05(2m)^2\Omega^{\frac{4}{3}}\Delta_\infty{}^2]^{n-1}, \quad (8)$$

where we have used

$$|G_0(\mathbf{r},\mathbf{r}',\omega)| = 2m/4\pi|\mathbf{r}-\mathbf{r}'|\,. \quad (9)$$

Equation (6) is absolutely convergent if

$$2m\Omega^{\frac{2}{3}}\Delta_\infty < 4.5\,, \quad (10)$$

a requirement met by specimens having maximum dimensions of several hundred to a thousand angstroms.

It should be pointed out that (6) diverges for bulk specimens, since the Bardeen–Cooper–Schrieffer energy gap equation[3] is not analytic at $\Delta = 0$.

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

The falloff of the pair amplitude in the normal metal can be calculated easily in the above case. Let the maximum dimension of the superconductor be d and let the distance from $\mathbf{r}$ to the center of the superconductor be $R \gg d$ [(cf. Fig. 1(b)]. We obtain

$$\begin{aligned} f^{(n)}(\mathbf{r},\mathbf{r},\omega) &= G_0(\mathbf{r}-\bar{\mathbf{r}}_1,\omega)i\Delta(\bar{\mathbf{r}}_1)G_0\cdots \\ &\quad\times G_0 i\Delta(\bar{\mathbf{r}}_{2n-1})G_0(\mathbf{r}-\bar{\mathbf{r}}_{2n-1},-\omega) \\ &= G_0(R,\omega)i\Delta(\bar{\mathbf{r}}_1)G_0\cdots G_0 i\Delta(\bar{\mathbf{r}}_{2n-1})G_0(R,-\omega) \\ &\quad\times[1+0(d/R)]\,, \end{aligned} \quad (11)$$

where the expansion of G_0 follows from (9). From (6), (9), and (11) we obtain

$$F(\mathbf{r},\mathbf{r},\omega) \propto R^{-2}\,. \quad (12)$$

For a plane boundary the calculation is similar. Let the normal metal with $V = 0$ occupy the half-space $z > 0$. Fourier transforming the x and y coordinates we obtain the one-dimensional analog of (11),

$$\begin{aligned} f^{(n)}(z,z',K,\omega) &= G_0(z-\bar{z}_1,K,\omega)i\Delta(\bar{z}_1)G_0\cdots \\ &\quad\times G_0 i\Delta(\bar{z}_{2n-1})G_0(z'-\bar{z}_{2n-1},K,-\omega) \\ &= e^{iq_+z}f^{(n)}(0^+,0^+,K,\omega)e^{iq_-z'} \end{aligned} \quad (13)$$

or

$$F(z,z,K,\omega) = \exp[i(q_+ + q_-)z]F(0^+,0^+,K,\omega)\,, \quad (14)$$

where

$$G_0(z,K,\pm|\omega|) = 2m\exp[iq_\pm|z|]/2iq_\pm\,, \quad (15)$$

$$q_\pm = (K^2 \pm 2m|\omega|)^{\frac{1}{2}} \approx \pm K + 2m|\omega|/2K\,, \quad (16)$$

$$2m|\omega| \ll K^2 \equiv 2mE_F - k_x^2 - k_y^2 = 2mE_F - k_\perp^2\,.$$

We do not know the form of $F(0^+,0^+,K,\omega)$, but we can approximate it by the bulk value, which is given by Gor'kov as[1]

$$F(\mathbf{k},\omega) = -i\Delta_\infty/(\omega^2 - \epsilon_\mathbf{k}^2 - \Delta_\infty^2)\,. \quad (17)$$

Fourier transforming this in k_z gives

$$F(z=0,K,\omega) = 2m\Delta_\infty/[4\pi K(\omega^2 - \Delta_\infty^2)^{\frac{1}{2}}]\,. \quad (18)$$

Substituting (18) in (14), we obtain

$$\begin{aligned} F(z,z,x=y=0,\omega) &= \int_0^\infty \frac{2m\Delta_\infty\exp[i(q_+ + q_-)z]k_\perp dk_\perp}{4\pi K(\omega^2 - \Delta_\infty{}^2)^{\frac{1}{2}}} \\ &= \frac{2m\Delta_\infty}{4\pi(\omega^2-\Delta_\infty^2)^{\frac{1}{2}}}\int_{-\infty}^{2mE_F}\exp[i(q_+ + q_-)z]\frac{dK^2}{2K}\,. \end{aligned} \quad (19)$$

Since the integrand goes to zero rapidly for $K^2 < 0$, we can replace the lower limit by zero. Expanding $q_\pm$ according to (16), we obtain[4]

[4] Because of the phonon cutoff, $F(\mathbf{k},\omega) \sim \omega^{-2}$ for large ω. Consequently the error in using (16) can be neglected.

$$F(z,z,x = y = t = 0) = (2\pi)^{-1}\int_{-\infty}^{\infty} d\omega$$
$$\times F(z,z,x = y = 0,\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} d\omega$$
$$\times \int_0^{k_F} KdK \exp\,[i(2m|\omega|z/K)]\frac{2m\Delta_\infty}{4\pi K(\omega^2 - \Delta_\infty^2)^{\frac{1}{2}}}$$
$$= \frac{2m\Delta_\infty k_F}{4\pi^2}\int_0^\infty \frac{d\omega}{(\omega^2 - \Delta_\infty^2)^{\frac{1}{2}}} B\left(\frac{2m\omega z}{k_F}\right), \qquad (20)$$

where

$$B(x) = ie^{ix}\int_0^\infty \left(\frac{t}{t + x}\right) e^{it}dt = e^{ix} - ix\,\mathrm{Ei}^+(ix)$$
$$\backsim -e^{ix}/x\,, \qquad x \gg 1\,. \qquad (21)$$

In the limit we obtain

$$F(z,z,x = y = t = 0) \propto B(2m\Delta_\infty z/k_F) \propto 1/z\,,$$
$$z > k_F/2m\Delta_\infty \approx 10^{-4}\mathrm{cm}\,. \qquad (22)$$

In calculating the z dependence of (20) at smaller distances, we must remember that by using the bulk value of F for $F(0^+,0^+)$ we neglect the effect of the change in energy gap near the edge of the superconductor.

This nonexponential falloff has been commented on by Falk.[5] It should be pointed out that this result is a consequence of choosing $V = 0$ in the normal metal. Since the pairing energy is zero, we have the limiting case of class II wave functions and the corresponding $1/z$ falloff.[6] In a metal having a repulsive interaction between electrons the positive potential energy might be expected to give rise to the exponential falloff characteristic of class I functions.

It might be added that metals having a repulsive electron–electron interaction will exhibit an energy gap in the neighborhood of a superconducting contact, following from (3) and the continuity of the wave function. This has been observed experimentally in tunneling experiments.[7]

This method is easily generalized to finite temperatures by the use of thermal Green's functions.[1] The above results are being extended to thin films and samples in which $V(r)$ takes both positive and negative values.

I am most thankful to Professor Leon Cooper for suggesting the above problem and for his many helpful suggestions.

[5] D. S. Falk, University of Maryland, Physics Department, Technical Report No. 315 (unpublished).
[6] E. C. Kemble, *Quantum Mechanics* (Dover Publications, Inc., New York, 1958), p. 85.
[7] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters 6, 686 (1961).

The Effect of Quasiparticle Damping on the Ratio between the Energy Gap and the Transition Temperature of Lead

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According to the BCS theory the ratio between the energy gap at zero temperature and the transition temperature (multiplied by the Boltzmann constant) is 3.5 in the weak coupling limit. However, experiments show that it increases to $\simeq$4.1 (for Pb) and $\simeq$4.6 (for Hg) as the electron–phonon coupling strength increases. Since nonresonant processes have been shown to decrease this ratio with increasing coupling strength,[1] we suggest that the quasi-particle damping gives rise to this phenomenon. Since the damping rate is greater at higher temperature, it reduces the transition temperature much more than the energy gap, thereby increasing the ratio.

In the calculation for lead, the electron–phonon interaction is written as

$$H' = \sum_{\substack{kK\\q\lambda}} \frac{1}{(2\omega_{q\lambda})^{\frac{1}{2}}} v(\mathbf{q} + \mathbf{K})(\mathbf{q} + \mathbf{K})\cdot \mathbf{e}_{q\lambda}c^*_{k+q+K}c_k a_{q\lambda}$$
$$+ \text{Hermitian conjugate},$$

where c_k annihilates an electron of quasi-momentum $\mathbf{k}$ and $a_{q\lambda}$ annihilates a phonon of momentum $\mathbf{q}$ (restricted to first Brillouin zone), polarization λ, and frequency $\omega_{q\lambda}$. The unit polarization vector $\mathbf{e}_{q\lambda}$ is as-

[1] G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters 8, 399 (1962).