# BERNOULLI POTENTIALS IN SUPERCONDUCTORS

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It is shown that the variation of electric potential with current density in superconductors depends on the band structure of the metal concerned and, contrary to the prediction of the free-electron model, can take either sign. At absolute zero the size of the effect can be calculated from the band structure alone, but its temperature variation is connected with the dependence of the order parameter on current density, and is harder to obtain.

In a recent Letter, Bok and Klein[1] report experiments in which they observe variations of the electronic work function for a superconductor due to the kinetic energy of the electrons in the current-carrying state. It is the purpose of this Letter to point out that the agreement which they obtain with a free-electron two-fluid model is surprising, for we shall show that the observed potentials depend on the detailed band structure of the metal concerned. In particular there is no reason to expect that the "penetration depth" deduced by their method should be close to the experimental value. We shall show that a form of compensation can occur in which the voltages observed may even reverse in sign.

In a superconductor the total chemical potential (the electrochemical potential), given by

$$\mu = \mu_c + eV, \tag{1}$$

where $\mu_c$ is the chemical potential referred to the local zero of the band energy, must be the same everywhere, even in the current-carrying state. In order to calculate $\mu_c$, Bok and Klein use a hydrodynamic model in which

$$\mu_c = \mu_0 + \tfrac{1}{2}mv_s^2, \tag{2}$$

where $\mu_0$ is the chemical potential when no current flows and $v_s$ is the velocity of the superfluid. (We have changed their notation slightly.) Instead of using a hydrodynamic model, we use a BCS model in the local electrodynamic limit and obtain a new relation between chemical potential and pair momentum which takes the band structure into account and replaces (2).

When a current is introduced into a superconductor there is, according to the BCS picture, a sideways shift of the occupied states in $k$ space. We can describe this by saying that the Fermi surface (or more strictly the "gap surface," the surface on which $u_k^2 = v_k^2 = \tfrac{1}{2}$) has moved. The one-electron states are still occupied in pairs, but their mean $k$ vector now takes a nonzero val-

ue $\vec{q}$, which for energetic reasons must be the same for all pairs. For a general band structure, however, the new gap surface will not be obtained from the old one merely by a translation $\vec{q}$, because it may be possible to reduce the energy of the system by redistributing the electrons around the surface while maintaining the pairing. To take account of this, we assume that the new surface can be obtained from the old one by a translation $\vec{q}$ and a relaxation through a second vector normal to the surface, $\vec{\delta}$, whose magnitude will vary with position but must be the same on opposite sides of the surface to maintain the pairing (see Fig. 1).

We then identify the new surface by applying the conditions (a) that the density of electrons must be conserved, and (b) that on the new surface the energy associated with the occupation of a given pair of states must be the same for all states.

The change in energy of a <u>normal one-electron state</u> on the gap surface produced by the displacement is

$$\delta\epsilon = \epsilon_i(q_i + \delta_i) + \tfrac{1}{2}\epsilon_{ij}(q_i + \delta_i)(q_j + \delta_j), \tag{3}$$

where

$$\epsilon_i = \partial\epsilon/\partial k_i \equiv \nabla_{ki}\epsilon, \quad \epsilon_{ij} = \nabla_{ki}\nabla_{kj}\epsilon,$$

and we have expanded to second order in $(\vec{q} + \vec{\delta})$. We now assume [see (1) below under "Notes"] that the <u>change</u> in the energy associated with occupation of a given pair of states <u>in the condensate</u> is

$$\alpha = (\delta\epsilon_1 + \delta\epsilon_2), \tag{4}$$

which by condition (b) must be the same for all pairs. Remembering that $\vec{\delta}$ must be second order in $\vec{q}$, we have to order $q^2$

$$\tfrac{1}{2}\alpha = \epsilon_i\delta_i + \tfrac{1}{2}\epsilon_{ij}q_iq_j = \hbar v_F\delta + \tfrac{1}{2}\epsilon_{ij}q_iq_j, \tag{5}$$

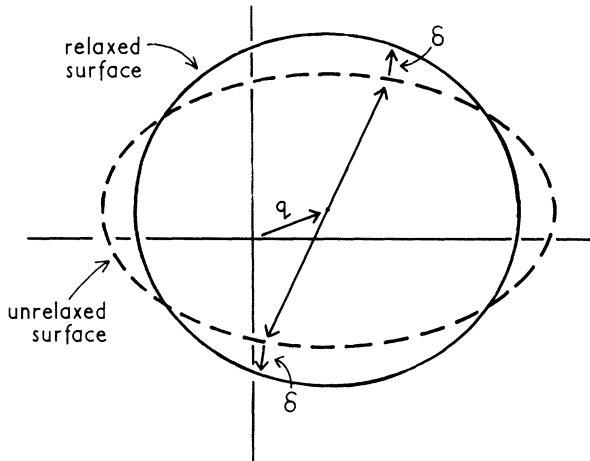since $\vec{\delta}$ is parallel to $\nabla_{\vec{k}}(\epsilon)$. Dividing by $\hbar v_F$, in-

FIG. 1. The vectors $\vec{q}$ and $\vec{\delta}$ which carry paired one-electron states on the original gap surface into paired states on the new gap surface.

tegrating over the Fermi surface, and using condition (a), we find

$$\alpha = \int_S \frac{(\epsilon_{ij}q_iq_j/\hbar v_F)dS}{\int_S(1/\hbar v_F)dS} . \qquad (6)$$

But $\alpha$, the change in the pair energy at the gap surface, is simply $2\delta(\mu_c)$, so that the change in contact potential is

$$V = -\frac{1}{2e}\int_S \frac{(\epsilon_{ij}q_iq_j/\hbar v_F)dS}{\int_S(1/\hbar v_F)dS} . \qquad (7)$$

The current density of the new distribution is

$$\vec{J} = \frac{e}{4\pi^3\hbar}\int_S[\vec{q}\cdot\nabla_{\vec{k}}(\epsilon)]dS, \qquad (8)$$

so that the experimentally measured quantity $V/J^2$ is given by

$$\frac{V}{J^2} = -\frac{(4\pi^3)^2}{2e^3}\frac{\int_S(\hbar v_F)^{-1}\epsilon_{ij}q_iq_j dS}{\int_S(\hbar v_F)^{-1}dS\{\int_S(\vec{v}_F\cdot\vec{q})dS\}^2} . \qquad (9)$$

For the common case of cubic symmetry, the denominator is independent of the orientation of the crystal axes with respect to $\vec{q}$, so that for a random polycrystalline aggregate the numerator may be averaged over orientations to give

$$\frac{V}{J^2} = -\frac{(12\pi^3)^2}{6e^3}\frac{\int_S(\hbar v_F)^{-1}\nabla_{\vec{k}}^2(\epsilon)dS}{\int_S(\hbar v_F)^{-1}dS\{\int_S v_F dS\}^2}$$

$$= \frac{(12\pi^3\hbar)^2}{2e^3S^2}\frac{\langle(v_F m^*)^{-1}\rangle}{\langle(v_F)^{-1}\rangle\langle v_F\rangle^2}, \qquad (10)$$

where $S$ is the total area of the Fermi surface. This reduces in the free-electron case to the usual result,

$$V/J^2 = -m/2n^2e^3. \qquad (11)$$

A simple situation in which the sign of the effect is reversed is the case of a Fermi surface consisting entirely of small spherical pockets of holes. If we adopt the usual convention for this case by speaking of the current as carried by positively charged holes of positive effective mass $m$ and density $n$, then (10) again reduces to (11), but the effect is reversed in sign because of the change in sign of $e$. In the general case the sign of the effect is determined by the sign of the integral containing $\nabla_{\vec{k}}^2(\epsilon)$, since the denominator is essentially positive.

It is worth pointing out that the condition for sign reversal in the present case is different from that for the ordinary Hall effect to reverse sign, which depends on the topology of the Fermi surface, but not on the second derivative of $\epsilon(\vec{k})$. An interesting case is that of cadmium, whose Fermi surface is quite close to a remapped free-electron sphere. The remapping happens to give it a large hole surface, thus producing a reversed normal Hall coefficient, but probably has comparatively little effect on the second derivative of $\epsilon(\vec{k})$ on most parts of the surface, so that the Bernoulli voltage should have the normal sign.

Notes. —(1) The assumption of Eq. (4) that $\alpha$ is given by $\delta\epsilon_1 + \delta\epsilon_2$ may be justified as follows: We insert the new one-electron energies $\epsilon_1, \epsilon_2$ into the BCS equations and make the usual assumption that $v_{kk'} = $const. This gives the standard relation $E^2 = (\epsilon-\mu_c)^2 + \Delta^2$ for the new pairs if we make the following identifications:

$$\epsilon = \tfrac{1}{2}(\epsilon_1 + \epsilon_2), \qquad (12)$$

$$E_1 = E + \tfrac{1}{2}(\epsilon_1-\epsilon_2); \quad E_2 = E - \tfrac{1}{2}(\epsilon_1-\epsilon_2), \qquad (13)$$

where $E_1, E_2$ are the new excitation energies. The gap surface is defined by the relation $\epsilon = \mu_c$, so we have

$$\delta\mu_c = \tfrac{1}{2}(\delta\epsilon_1 + \delta\epsilon_2) = \tfrac{1}{2}\alpha = -eV \qquad (14)$$

as before.

(2) Our argument, which uses a $k$-space description of the current-carrying state, is only valid in the London limit. It is known how nonlocal effects such as long coherence lengths and short mean free paths affect the current response of a superconductor. Since they change the current, they must also change the kinetic energy

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and hence the chemical potential, but we do not know how to calculate this effect, which is likely to be important in practice.

(3) A further correction to the simple hydrodynamic result comes from the fact that in the superconducting state the occupation of one-electron states $u^2(\epsilon)$ does not drop abruptly to zero at the gap surface, but falls gradually over a range of energies of order $\Delta$. If now the density of states near the gap surface varies with energy, and if $\Delta$ also happens to vary with $\vec{q}$, there will be a further change in the chemical potential somewhat analogous to the shift which takes place with temperature in a normal metal. We find after some calculation that (6) is then replaced by

$$\alpha = \left[ \int_S \frac{\epsilon_{ij} q_i q_j}{\hbar v_F} dS - \int_S \left( \ln \frac{2\hbar\omega_c}{\Delta} - \frac{1}{2} \right) \left\{ \frac{\delta(\Delta^2)}{(\hbar v_F)^2} \right\} \left( \nabla^2 \epsilon - \frac{2 d^2 \epsilon}{dk_n^2} \right) \frac{dS}{\hbar v_F} \right] [\int_S (\hbar v_F)^{-1} dS]^{-1} \tag{15}$$

for a weak-coupling superconductor. The correction term is evidently serious unless

$$\delta(\Delta^2) \ll (\hbar q v_F)^2. \tag{16}$$

The change of $\Delta$ with $\vec{q}$ can be estimated near $T_c$ using the Ginzburg-Landau theory, and in this regime we find that the correction is always serious. At low temperatures, however, where there are negligibly few excitations, $\Delta$ can only change through the $k$ dependence of $V_{kk'}$. We would expect this to be extremely small ($V_{kk'}$ is taken as constant in the BCS model), so that our original result (6) is probably valid at sufficiently low temperatures.

(4) Bok and Klein argue that in a superconductor the Lorentz force on the electron fluid cannot be transmitted to the lattice by collisions, and must therefore be transmitted by an electric field. They deduce that the superconducting Hall constant depends only on the lattice charge density and will be independent of temperature. We would comment as follows:

(i) The argument appears to apply only in a strictly free-electron model. In a real metal electromagnetic forces on the electrons may sometimes be transmitted to the lattice without the mediation of real scattering processes. (This is obviously the case in a full band, for instance.) There seems to be no reason to exclude this possibility for superconductors. In fact, there is no unique way of defining the "lattice charge" in a real metal.

(ii) The argument only applies at $T = 0$. At finite temperatures some of the electromagnetic force acts directly on the electronic excitations and may be transmitted to the surface of the specimen by collisions (cf. a gas in equilibrium in a gravitational field).

(iii) The temperature dependence of the effect could be calculated directly by a natural extension of our method. The argument leading to (5) as given in Note (1) is independent of temperature, and it is only Eq. (8) and the charge conservation condition which require modification. The required modification to (8) which gives the current density is well known. The charge conservation relation must be corrected to allow for variations in the chemical potential with $\Delta$ and with temperature, but these can easily be written down. As discussed above, the only difficulty is to estimate the dependence of $\Delta$ on $\vec{q}$ for real superconductors at finite temperatures.

[1]J. Bok and J. Klein, Phys. Rev. Letters **20**, 660 (1968).