On the Thermodynamic Stability of Odd-Frequency Superconductors

R. Heid

Department of Physics, The Ohio State University, Columbus, Ohio 43210

Abstract

The thermodynamic stability of odd-frequency pairing states is investigated within an Eliashberg-type framework. We find the rigorous result that in the weak coupling limit a continuous transition from the normal state to a spatially homogeneous odd-in-ω superconducting state is forbidden, irrespective of details of the pairing interaction and of the spin symmetry of the gap function. For isotropic systems, it is shown that the inclusion of strong coupling corrections does not invalidate this result. We discuss a few scenarios that might escape these thermodynamic constraints and permit stable odd-frequency pairing states.

Keywords: Superconductivity, Theory, Thermodynamic Properties

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I. INTRODUCTION

The puzzling physical properties of cuprate and heavy-fermion superconductors have motivated theoretical investigations of new classes of superconductivity which are characterized by unconventional symmetries of the gap function $\Delta(k, \omega_n)$. A prominent example is the odd-frequency superconducting state where $\Delta$ changes sign under inversion of frequency, originally considered by Berizinskii in a model for triplet superfluidity in $^3$He [1]. This idea was picked up by Balatsky and Abrahams who proposed a new class of odd-in-$\omega$ singlet superconductors which are odd under parity as well due to the Pauli principle [2]. A possible microscopic realization of odd-frequency triplet pairing has been discussed by Coleman et al. in the context of heavy-fermion compounds [3].

The physical properties of these unconventional pairing states are rather unusual. Because the equal-time gap vanishes, the order parameter of the condensed state is related to the expectation value of a composite operator [4,5]. In case of a singlet pairing, the quasiparticle spectrum turns out to be gapless [2,4]. However, some concern has recently been raised with regard to the stability of odd-frequency pairing. As argued by Coleman et al., a uniform s-wave triplet odd-in-$\omega$ state should generically exhibit a negative Meissner effect and is therefore unstable with respect to a spatial modulation of the order parameter [3]. Additional support for a negative Meissner effect comes for calculations of the Meissner kernel using normal and anomalous Green's functions, whereas a positive Meissner effect is found within the composite-operator description [4]. Furthermore, uniform odd-frequency singlet pairing seems to contradict the requirements of causality and stability [4].

In this paper we intend to shed additional light on the question of stability of an odd-in-$\omega$ superconductor. This is achieved by examining the pairing induced change in the thermodynamic potential. The main result is that under quite general circumstances a continuous transition from a normal state into a spatially homogeneous condensed state is ruled out on thermodynamic grounds. This suggests that odd-frequency pairing cannot be realized in a uniform ground state.
The derivation of the above mentioned statement is presented in the next section. After introducing the formalism in Section IIA, we first consider the weak coupling limit, where the main ideas involved in the derivation can be presented in a very simple form (Section IIB). However, studies of the strong-coupling gap equation show that odd-frequency solutions often involve substantial renormalizations in the normal channel \[4,7\]. It is therefore important to include strong coupling corrections in the stability analysis. In Section IIC, we demonstrate that, at least for isotropic systems, strong coupling corrections are ineffective in stabilizing a uniform odd-frequency state. Implications of these results are discussed in Section III.

II. STABILITY ANALYSIS

A. Formalism

We work within the framework of Fermi liquid theory. The following assumptions are made: (i) no spin-orbit coupling, (ii) pairing occurs in a quasiparticle band described by spin-independent energies \(\epsilon_k\) (measured from to the chemical potential), (iii) the low-temperature behavior can be described by a spin- and frequency-dependent effective interaction \(V(\sigma_1k_1,\sigma_2k_2|\sigma_3k_3,\sigma_4k_4)\) where \(\sigma_i\) are spin indices and we have used a four-vector notation, \(k = (k,\omega_n)\). Fermi statistics implies that \(V\) is antisymmetric with respect to the first two and last two \((\sigma,k)\) index pairs, respectively. The only further restrictions imposed on the functional form of \(V\) come from the conservation of total spin, energy and momentum \((\sum_{i=1}^{4} k_i = 0)\), and from the hermiticity of the Hamiltonian which implies

\[
V^*(\sigma_1k_1,\sigma_2k_2|\sigma_3k_3,\sigma_4k_4) = V(\sigma_4\bar{k}_4,\sigma_3\bar{k}_3|\sigma_2\bar{k}_2,\sigma_1\bar{k}_1)
\]  

where \(\bar{k} = (k,-\omega_n)\).

For a spatially homogeneous pairing state, the anomalous Green’s functions are defined as
\[
F_{\alpha\sigma'}(k) = \int_0^\beta d\tau e^{i\omega_n \tau} < T^\alpha_\tau \psi_{k\sigma}(\tau) \psi_{-k\sigma'}(0) > ,
\]
\[
\hat{F}_{\alpha\sigma'}(k) = \int_0^\beta d\tau e^{i\omega_n \tau} < T^\alpha_\tau \psi^{\dagger}_{-k\sigma}(\tau) \psi^{\dagger}_{k\sigma'}(0) > ,
\]
(2)

which are related by \( \hat{F}_{\alpha\sigma'}(k) = F^*_{\alpha'\sigma}(\bar{k}) \). Fermi statistics requires \( F_{\alpha\sigma'}(k) = -F_{\alpha'\sigma}(-k) \).

Using a matrix notation, the Gor’kov equations are given by

\[
\begin{align*}
[(i\omega_n - \epsilon_k)\mathbf{1} - W(k)]G(k) &= \mathbf{1} - \phi(k)\hat{F}(k), \\
[(i\omega_n + \epsilon_k)\mathbf{1} + W(-k)]\hat{F}(k) &= -\phi^\dagger(\bar{k})G(k).
\end{align*}
\]
(3)

These equations contain the normal and anomalous parts of the electron self-energy defined by

\[
W_{\sigma_1\sigma_2}(k) = \frac{1}{\beta} \sum_{p\sigma_3\sigma_4} 2V(\sigma_1 k, \sigma_4 p|\sigma_3 p, \sigma_2 k)G_{\sigma_3\sigma_4}(p)
\]
\[
\phi_{\sigma_1\sigma_2}(k) = \frac{1}{\beta} \sum_{p\sigma_3\sigma_4} V(\sigma_1 k, \sigma_2 - k|\sigma_3 p, \sigma_4 - p)F_{\sigma_3\sigma_4}(p).
\]
(4)

As a consequence of the antisymmetry of \( V \), the relation \( \phi_{\sigma\sigma'}(k) = -\phi_{\sigma'\sigma}(-k) \) holds.

The following stability analysis of the odd-frequency superconducting state makes use of a general expression for the change in the thermodynamic potential due to the two-body interaction \( V \) [8]

\[
\delta\Omega = \frac{1}{\beta} \int_0^1 dg \sum_k tr\{(i\omega_n - \epsilon_k)G(k) - \mathbf{1}\} g.
\]
(5)

The trace is taken over spin indices, and the index \( g \) indicates that the quantities in the bracket correspond to a system with a scaled interaction \( gV \). This formula is not restricted to weak coupling and is applicable even in the case of a critical lower coupling strength. We assume that the interaction potential \( V \) allows a certain type of solution of the gap equations (3) and (4), and examine its thermodynamic stability with respect to the normal state. It is now useful to distinguish between weak and strong coupling.
B. Weak coupling

The weak coupling approximation is obtained by neglecting the self-energy contributions in the normal channel, \( W = 0 \), in which case \( \delta \Omega \) equals the difference between the normal and superconducting state. Combining (3) and (5), we obtain

\[
\delta \Omega = \frac{1}{\beta} \int_0^1 \frac{dg}{2g} \sum_k \text{tr} \{ \phi(k) \bar{F}(k) \} g
\]

\[
= \frac{1}{\beta} \int_0^1 \frac{dg}{2g} \sum_k \text{tr} \left\{ \left[ (\omega_n^2 + \epsilon_k^2) \mathbf{1} + \phi^\dagger(\bar{k}) \phi(k) \right]^{-1} \phi^\dagger(\bar{k}) \phi(k) \right\} g. \quad (6a)
\]

Let us now consider a continuous phase transition. For temperatures close to \( T_c \) we can neglect the term proportional to \( \phi^2 \) in the denominator

\[
\delta \Omega = \frac{1}{\beta} \int_0^1 \frac{dg}{2g} \sum_k \text{tr} \left\{ \phi^\dagger(\bar{k},-\omega_n) \phi(k,\omega_n) \right\} g. \quad (7)
\]

In this form the sign of \( \delta \Omega \) can be determined by solely relying on symmetry properties of the gap function. There are two distinct cases:

1. \( \phi(k,-\omega_n) = \phi(k,\omega_n) \), i.e. \( \phi \) is even in \( \omega \). Because \( \phi^\dagger(k,-\omega_n) \phi(k,\omega_n) \) is a positive definite matrix (for all \( g \)), it follows that \( \delta \Omega < 0 \) and the paired state is stable with respect to the normal state.

2. \( \phi(k,-\omega_n) = -\phi(k,\omega_n) \), i.e. \( \phi \) is odd in \( \omega \). This implies \( \delta \Omega > 0 \) showing that in this case the condensed state does not fulfill the thermodynamic stability criterion.

Consequently, a second-order transition to a spatially homogeneous, odd-frequency superconducting state is forbidden. Furthermore, in the weak coupling limit, this conclusion does not depend on the details of the pairing interaction and is valid for singlet and triplet pairing.

C. Strong coupling

We now extend the above given arguments to incorporate strong coupling corrections. In this case, no derivation with a generality similar to the weak coupling limit exists. However,
we show that the same conclusions still hold for the class of isotropic models. This class is
defined by

(i) isotropic quasiparticle energies, \( \epsilon_k = \epsilon_{|k|} \), and particle-hole symmetry;

(ii) a general spin-dependent interaction \( V(12|34) = \Gamma(1234) - \Gamma(1243) \) with

\[
\Gamma(1234) = \left[ \Gamma_C(k_1 - k_3) \right. \\
\left. + \Gamma_S(k_1 - k_3) \sum_i \sigma_i \sigma_1 \sigma_2 \sigma_4 \right] \delta_{k_1,k_3,k_4,k_2}
\]  

(8)

where \( 1 \equiv (k_1 \sigma_1) \), \( \sigma_i = x,y,z \), and \( \sigma^i \) denote Pauli matrices. \( \Gamma_C \) and \( \Gamma_S \) are
functions symmetric in frequency and rotationally invariant in momentum space;

(iii) negligible \(|k|\)-dependence of \( \Gamma \) and the self-energy in the vicinity of the Fermi surface.

The same type of interaction has been used in the work of Abrahams et al. [7].

For singlet pairing the normal self-energy is diagonal in spin-space, \( W(k) = i\omega_n Z(k) \mathbf{1} \), and the gap function \( \Delta \) is given by \( \phi(k) = i\sigma^y Z(k) \Delta(k) \). Under these conditions, (5) is
equivalent to

\[
\delta \Omega = - \int_0^1 \frac{dg}{g} \left\{ \mathcal{N}(0) \frac{\pi}{\beta} \sum_n \int \frac{d\Omega_k}{4\pi} \frac{\omega_n^2(Z(\hat{k},\omega_n) - 1) + Z(\hat{k},\omega_n)\Delta(\hat{k},\omega_n)\Delta^*(\hat{k},-\omega_n)}{\sqrt{\omega_n^2 + \Delta(\hat{k},\omega_n)\Delta^*(\hat{k},-\omega_n)}} \right\}_g
\]

(9)

where \( \mathcal{N}(0) \) is the density-of-states per spin at the Fermi energy, and \( \hat{k} \) is a vector on the
Fermi surface. The renormalization factor takes the form

\[
Z(\hat{k},\omega_n) = 1 + \frac{1}{\omega_n \beta} \sum_m \int \frac{d\Omega_p}{4\pi} \frac{\omega_m}{\sqrt{\omega_m^2 + \Delta(\hat{p},\omega_m)\Delta^*(\hat{p},-\omega_m)}}
\]

(10)

Here, \( \gamma = 2\mathcal{N}(0)(\Gamma_C^2 + 3\Gamma_S^2) \) is the effective interaction entering the normal self-energy.

The possibility of a second order transition from the normal state into the superconducting
state is determined by the sign of the second order term in an expansion of \( \delta \Omega \) in the
gap function \( \Delta \). Using (10) to replace \( Z \), one finds

\[
\delta \Omega_2 = - \int_0^1 \frac{dg}{g} \left\{ \mathcal{N}(0) \frac{\pi}{\beta} \sum_n \int \frac{d\Omega_k}{4\pi} \frac{\Delta(\hat{k},\omega_n)\Delta^*(\hat{k},-\omega_n)}{\omega_n} \right. \\
+ \frac{\pi^2}{\beta^2} \sum_{nm} \int \frac{d\Omega_k}{4\pi} \int \frac{d\Omega_p}{4\pi} \frac{\omega_n}{\omega_n} \frac{\omega_m}{\omega_m} \\
\left. \times \left( \frac{\Delta(\hat{k},\omega_n)\Delta^*(\hat{k},-\omega_n)}{\omega_n^2} - \frac{\Delta(\hat{p},\omega_m)\Delta^*(\hat{p},-\omega_m)}{\omega_m^2} \right) \right\}_g
\]

(11)
Because $\gamma$ is symmetric with respect to an exchange $(\hat{k}\omega_n) \leftrightarrow (\hat{p}\omega_m)$, the last term vanishes when summed over frequencies, and we are left with

$$
\delta \Omega_2 = - \int_0^1 \frac{dg}{g} \left\{ \mathcal{N}(0) \frac{\pi}{\beta} \sum_n \int \frac{d\Omega_k}{4\pi} \frac{\Delta(\hat{k},\omega_n)\Delta^*(\hat{k},-\omega_n)}{|\omega_n|} \right\}_g
$$

The expression for $\delta \Omega_2$ is very similar to (7), and application of the same reasoning as in the previous subsection shows that strong coupling corrections cannot stabilize odd-in-$\omega$ pairing for the class of models considered. This result is in agreement with the conclusions obtained by Dolgov and Losyakov [6].

The present derivation is not restricted to singlet pairing, but holds for unitary triplet pairing, too, where the normal self-energy retains the same spin-diagonal form, and $\phi(k) = iZ(k)(d(k) \cdot \vec{\sigma})\sigma_y$ with $d(k) \times d^*(\bar{k}) = 0$. In this case, the product $\Delta(k)\Delta^*(\bar{k})$ is simply replaced by the scalar product $d(k) \cdot d^*(\bar{k})$ in (9)-(12). No similar derivation seems to exist, however, for a nonunitary triplet pairing ($d(k) \times d^*(\bar{k}) \neq 0$).

### III. DISCUSSION

The result obtained in the previous section emphasizes some constraints imposed by thermodynamics which must be fulfilled by any realization of these unconventional superconducting states. However, our derivation should not be mistaken as a proof of the nonexistence of odd-frequency pairing in general. As mentioned before, it requires the applicability of an Eliashberg-type approach. Moreover, there are certain scenarios which are not covered by our analysis, and may allow stable odd-in-$\omega$ states.

First, it is possible that in a system with large anisotropy, strong coupling corrections are more effective in producing a stable uniform odd-frequency superconducting ground state. Second, our analysis concentrated on second order transitions only, but does not exclude a first order transition. This possibility is easiest seen for singlet pairing in the weak coupling limit (i.e. $\phi(k) = i\sigma_y\Delta(k)$). In the odd-in-$\omega$ case, the $\Delta^2$ term in the denominator of (6b) is negative, leading to
\[ \delta \Omega = \frac{1}{\beta} \int_{0}^{1} \frac{dg}{g} \sum_{k} \left\{ \frac{|\Delta(k)|^2}{\omega_n^2 + \epsilon_k^2 - |\Delta(k)|^2} \right\} g. \]  

(13)

If the sign in the denominator is changed for a sufficiently large \( k \)-region, the pairing state might be stabilized.

A third scenario is based on the idea of a spatial inhomogeneity of the pairing amplitude. Here, the Cooper pairs acquire a finite center-of-mass momentum \( \mathbf{q} \), which describes the modulation of the order parameter on the lattice. This type of pairing has recently been discussed in more detail in the context of heavy fermion superconductors, and is thought to be driven by the negative Meissner stiffness of the homogeneous odd-in-\( \omega \) state, which favors a coiling of the order parameter phase [3,9].

It is easy to connect this picture to the thermodynamic stability consideration. Let \( \delta \Omega(\mathbf{q}) \) be the potential difference between the normal state and a superconducting state with a finite total momentum \( \mathbf{q} \) of the electron pairs. The Meissner stiffness is proportional to the coefficients of the gradient terms in a Ginzburg-Landau expansion of the free energy, and is therefore related to the second derivative of \( \delta \Omega(\mathbf{q}) \) with respect to \( \mathbf{q} \). The positive Meissner stiffness found for a homogeneous phase of an even gap superconductor thus corresponds to a minimum of \( \delta \Omega(\mathbf{q}) \) at \( \mathbf{q} = 0 \). The results of the previous section, in conjunction with a negative Meissner stiffness obtained for the uniform odd-in-\( \omega \) state, suggests that in this case \( \delta \Omega(\mathbf{q}) \) is instead maximal at \( \mathbf{q} = 0 \). Consequently, the global minimum of \( \delta \Omega(\mathbf{q}) \) occurs at a finite momentum \( \mathbf{q}_{\min} \), which defines an odd superconducting state with a positive Meissner stiffness. This state is stable with respect to the normal state if \( \delta \Omega(\mathbf{q}_{\min}) < 0 \), a necessary condition which may be violated even for interactions attractive in the odd-frequency pairing channel (i.e. which allows odd-in-\( \omega \) solutions of the gap equations). This contrasts the even-in-\( \omega \) case, where a homogeneous phase is always stable for an attractive pairing potential.

One should keep in mind that the given discussion solely addresses the thermodynamic stability of odd-in-\( \omega \) states with respect to the normal state. States which are stable according to this criterion do not necessarily correspond to the ground state, because competing
even-frequency states might possess even lower free energies. This question can only be answered when a specific interaction potential is given.

In summary, we have shown that the thermodynamic stability criterion puts severe restrictions on the occurrence of a continuous phase transition to a spatially homogeneous odd-in-$\omega$ superconducting state. This result strongly suggests that any realistic model of this unconventional pairing requires a spatial modulation of the order parameter on an atomic scale from the very beginning.

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