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TOPICAL REVIEW

Unconventional superconductivity

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Abstract. We present a review of the basic theoretical ideas concerning unconventional superconductors. These are superconductors with an order parameter which breaks the rotational symmetry of the normal-state crystal; in some cases, time-reversal symmetry is broken as well. The resulting novel broken-symmetry state should display many unusual properties, which can be analysed at a variety of theoretical levels. We pay particular attention to the Ginzburg–Landau type of theory, and to the more microscopic theory of a superfluid Fermi liquid.

1. Introduction

In this article we will review the basic theoretical ideas concerning unconventional superconductivity. There has been a great development of such ideas in recent years [1, 2]; this development has been driven by exciting experimental discoveries of new classes of superconducting materials. These classes include the high-T_c oxides [3], the heavy-fermion metals [4–6], and the fullerene compounds [7, 8].

The term 'unconventional' refers to superconductors with order parameters which have a lower rotational symmetry than the normal-state crystal. This broken rotational symmetry may occur in real space, or in both real space and spin space, as will be illustrated in this article. This definition of unconventional is based, then, on symmetry, not on the mechanisms responsible for producing the superconductivity. A fundamental goal for physicists is to elucidate the consequences of these novel broken-symmetry states.

Classifying and discussing superconductors on the basis of the symmetry of their order parameters has some important advantages. The Ginzburg–Landau (GL) type of theory can be developed in great detail, allowing definite predictions of experimental properties to be made. If certain assumptions are valid, such as the normal state being a normal Fermi liquid, then theory at a more microscopic level may be worked out, predicting in greater detail the properties of a superconductor with an order parameter of a certain symmetry. Just as for the GL theory, this can be done without specifying the underlying mechanism.

An analogy to this situation in another area of condensed-matter physics is the following. Consider a material forming a BCC crystal. Without considering the mechanisms responsible for this particular broken-symmetry state (i.e. the BCC crystal) we can discuss with varying degrees of precision such properties as the x-ray diffraction pattern, the phonon spectrum, and the electronic energy bands.

When the order parameter has a reduced symmetry, so, in general, will many properties of the superconducting state. For example, in a cubic crystal whose order parameter has a lower symmetry, the superfluid density tensor may not have cubic symmetry. In a sense, effects such as these are perhaps obvious. However, recent theoretical work has led us to

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expect a variety of subtle and surprising effects when the order parameter is unconventional; we will pay particular attention to such effects in this review.

For example, the GL theory of an unconventional superconductor can be much richer than that of a conventional one, because the order parameter can have more internal degrees of freedom. These degrees of freedom can induce intricate behaviour, for example at H_{c2}, or in the vortex core region; they even lead to the possibility of an unexpected instability. Order parameters which break time-reversal symmetry are also possible. We can then have unusual supercurrents and their associated magnetic fields, which have no analogue in the conventional case. Finally, we mention that scattering by ordinary, nonmagnetic impurities leads to an array of novel phenomena when the order parameter is unconventional.

The plan of this paper is as follows. Section 2 contains a general discussion of the order parameter for a superconductor, paying particular attention to its behaviour under spin rotations, space rotations, and time reversal. A clear grasp of these points is essential to understanding these novel broken-symmetry states. In section 3 the fundamental ideas of the Ginzburg–Landau theory are explained. One particular case of the GL theory is covered in more detail in section 4, to illustrate the new features which can arise when the order parameter is unconventional. In section 5 we briefly review the microscopic theory of a superconducting Fermi liquid. Some specific calculations are then discussed, with an emphasis on the new phenomena typical of unconventional superconductors.

2. The order parameter

2.1. Definition

The order parameter for a superconductor can be taken to be the energy gap, or off-diagonal component of the self-energy, $\Delta_{\alpha\beta}(\boldsymbol{k})$. It is a 2×2 matrix in spin space, and a function of $\boldsymbol{k}$ in momentum space, with the transformation properties of a two-electron wavefunction [9, 10]. The Pauli principle forces Δ to be antisymmetric:

$$\Delta_{\alpha\beta}(\boldsymbol{k}) = -\Delta_{\beta\alpha}(-\boldsymbol{k}). \tag{1}$$

Two points are important to make.

- For systems with spin–orbit coupling, we may regard the subscripts α, β as pseudospin labels [9, 10]. When a crystal has inversion symmetry, its electronic eigenstates for a given $\boldsymbol{k}$ are still doubly degenerate, even in the presence of spin–orbit coupling. It is convenient to take the subscripts as labels of these two degenerate states. We may always select linear combinations of these two states such that under spin rotations of the point group, $\Delta_{\alpha\beta}$ rotates according to the usual spin-rotation matrices. This point arises in the context of the heavy-fermion superconductors, which have strong spin–orbit coupling.
- Another choice for an order parameter is the quantity $\Psi_{\alpha\beta}(\boldsymbol{k}) = \langle a_{\boldsymbol{k}\alpha} a_{-\boldsymbol{k}\beta} \rangle$. This choice is perhaps best if one wants to make the most minimal assumptions as to the microscopic description of the superconducting state [11]. All the GL theory developed in this chapter goes through with this choice for the order parameter.

We can always write $\Delta_{\alpha\beta}$ in the following form:

$$\Delta_{\alpha\beta}(\boldsymbol{k}) = \mathrm{i}\sigma^{y}_{\alpha\beta}\Delta(\boldsymbol{k}) + \mathrm{i}\boldsymbol{d}(\boldsymbol{k}) \cdot \boldsymbol{\sigma}_{\alpha\mu}\sigma^{y}_{\mu\beta} \tag{2}$$

where $\sigma^i_{\alpha\beta}$ denotes a Pauli matrix, $\Delta(-\boldsymbol{k}) = \Delta(\boldsymbol{k})$, and $\boldsymbol{d}(-\boldsymbol{k}) = -\boldsymbol{d}(\boldsymbol{k})$. The singlet part of the order parameter is given by $\Delta(\boldsymbol{k})$, while the triplet part is given by $\boldsymbol{d}(\boldsymbol{k})$. The $\boldsymbol{d}$-vector notation simply reorganizes the three triplet states. Instead of listing the coefficients of $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, and $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$, we group them as follows [12]:

$$d_x \Longleftrightarrow -(|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle) \tag{3}$$

$$d_y \Longleftrightarrow \mathrm{i}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle) \tag{4}$$

$$d_z \Longleftrightarrow (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle). \tag{5}$$

The quantity $\boldsymbol{d}$ then transforms as a vector under spin rotations.

The effect of time reversal on the order parameter is also important to study [9, 10]. Under time reversal, $\Delta(\boldsymbol{k})$ becomes $\Delta^*(\boldsymbol{k})$. Thus, if there exists a constant α such that

$$\Delta^*(\boldsymbol{k}) = \exp(\mathrm{i}\alpha)\Delta(\boldsymbol{k}) \tag{6}$$

then we say that the order parameter does not break time-reversal symmetry. If no such α can be found, then we say that Δ does break time-reversal symmetry. Note that with this definition, multiplying the order parameter by a $\boldsymbol{k}$-independent phase factor does not affect whether or not it breaks time-reversal symmetry. Similar considerations hold for $\boldsymbol{d}(\boldsymbol{k})$: if for some α we have

$$\boldsymbol{d}^*(\boldsymbol{k}) = \exp(\mathrm{i}\alpha)\boldsymbol{d}(\boldsymbol{k}) \tag{7}$$

then we say that $\boldsymbol{d}$ is invariant under time reversal.

2.2. The residual symmetry group

Even if an unconventional order parameter is not invariant under all of the operations of the normal-state point group, it may still be invariant under some subset of those operations. Knowledge of this subset, called the residual symmetry group, may permit much understanding of the properties of the superconductor without any further specification of the form of the order parameter [10, 13, 15]. To investigate this point further, it is instructive to enlarge the scope of the term 'operation'. Besides the usual rotations, inversions and reflections, we can consider the operations of time reversal and of multiplying the order parameter by a phase factor. For example, it can prove useful to know that an order parameter is left invariant if we perform a certain rotation, and then multiply it by $\exp(\mathrm{i}\pi/3)$.

For a given crystal structure, theoretical arguments can be used to elucidate the possible residual symmetry groups. For a triplet order parameter with negligible spin–orbit coupling, the full symmetry group of the normal state is taken to be the following:

$$\mathcal{G} = \mathrm{SO}(3) \times G \times \mathrm{E} \times \mathrm{U}(1). \tag{8}$$

These correspond to the various operations that we may perform on the order parameter. SO(3) is the full spin-rotation group, G is the point group of the crystal (acting on $\boldsymbol{k}$), E is the two element group containing the time-reversal operator and the identity, and U(1) is the unitary group (i.e. multiplying the order parameter by a constant phase factor).

For triplet order parameters with strong spin–orbit coupling, and for spin-singlet order parameters in all cases, the proper choice for $\mathcal{G}$ is

$$\mathcal{G} = G \times \mathrm{E} \times \mathrm{U}(1). \tag{9}$$

(For singlet order parameters with no spin–orbit coupling, we could include SO(3) in $\mathcal{G}$, but it is not necessary, since the order parameter will simply be invariant under all spin rotations.) For any particular $\mathcal{G}$, then, there are two questions that we can ask: (i) what are

the possible subgroups H of $\mathcal{G}$ and (ii) for a given H, what general properties of the order parameter may we ascertain?

The answer to (i) has been discussed by several authors, and we refer the reader to these articles [10, 13–15]. One type of answer to (ii) is that for certain subgroups H it is possible to prove that the order parameter must vanish on certain domains in $\boldsymbol{k}$-space [10, 13–15]. We can use a simple example to show how arguments of this type work. Consider the spherical harmonic $Y_{11}(\hat{\boldsymbol{k}})$. Suppose that we did not know the detailed form of this function, but that we did know that under rotations $\mathcal{R}(\hat{\boldsymbol{z}}, \alpha)$ about the $\hat{\boldsymbol{z}}$-axis, it behaved as follows:

$$Y_{11}(\mathcal{R}(\hat{\boldsymbol{z}}, \alpha)\hat{\boldsymbol{k}}) = \exp(\mathrm{i}\alpha) Y_{11}(\hat{\boldsymbol{k}}). \tag{10}$$

That is, a rotation about the $\hat{\boldsymbol{z}}$-axis by α multiplies Y_{11} by the factor $\exp(\mathrm{i}\alpha)$. Then, for the specific choice of $\hat{\boldsymbol{k}} = \hat{\boldsymbol{z}}$ we have, for all values of α,

$$Y_{11}(\hat{\boldsymbol{z}}) = \exp(\mathrm{i}\alpha) Y_{11}(\hat{\boldsymbol{z}}). \tag{11}$$

Thus we see that $Y_{11}(\hat{\boldsymbol{k}})$ must vanish for $\hat{\boldsymbol{k}} = \pm\hat{\boldsymbol{z}}$. As we will see, zeros of the order parameter are important in microscopic calculations of quantities such as the density of states.

2.3. The form of the order parameter

In this section, we discuss how the theory of group representations [16] can be used to analyse the form of the order parameter. This formalism leads in a natural way to the Ginzburg–Landau theory discussed later in this article. To start, we note that the order parameter can always be expanded in terms of basis functions of the irreducible representations of the crystalline point group. For a singlet order parameter we may write:

$$\Delta(\boldsymbol{k}) = \sum_{\mu j} \eta_{\mu j} \phi_{\mu j}(\boldsymbol{k}). \tag{12}$$

Here $\phi_{\mu j}$ denotes the jth basis function of the irreducible representation μ. Thus, the set of complex numbers $\eta_{\mu j}$ specifies the order parameter.

One may ask what determines the form of the basis functions. Recall that under a group operation $\mathcal{R}$ we have

$$\phi_{\mu i}(\mathcal{R}\boldsymbol{k}) = \sum_{j} D^{\mu}_{ij}(\mathcal{R}) \phi_{\mu j}(\boldsymbol{k}) \tag{13}$$

where $D^{\mu}_{ij}(\mathcal{R})$ is the matrix representing the operation $\mathcal{R}$ in the μ-representation. Within this constraint, however, there are many possible choices for the $\phi_{\mu i}$. As we shall see, the detailed $\boldsymbol{k}$-dependence of the pairing interaction determines the particular form of the basis function. This pairing interaction contains all the complicated microscopic physics (i.e. electron–phonon, electron–electron interactions) which gives rise to the Cooper pairing. In general, then, it is an ambitious project to determine the detailed form of the $\phi_{\mu i}$.

A recent paper [17] nicely clarifies the extent to which these basis functions are arbitrary. Consider a particular irreducible representation, ν, which is ℓ-dimensional. Then, there exists a set of functions $\psi^{a}_{\nu i}$ such that we can write

$$\phi_{\nu i}(\boldsymbol{k}) = \sum_{a=1}^{\ell} F^{ia}(\boldsymbol{k}) \psi^{a}_{\nu i}(\boldsymbol{k}) \tag{14}$$

where the coefficients $F^{ja}(\boldsymbol{k})$ are invariant under all operations of the crystal point group. So, the $\psi^{a}_{\nu j}$ can be specified, and our ignorance is packaged in the functions F^{ja}, which

must however have the complete crystal symmetry. Yip and Garg tabulate these functions ψ for some particular point groups [17].

As a concrete example of what this means, suppose we have a crystal with the D_{4h} point group, and that in the sum over μ in (12) only the (two-dimensional) E_g representation occurs. (As we shall see, in many situations only one representation in fact occurs.) Then we may write

$$\Delta(\boldsymbol{k}) = \eta_1\phi_1(\boldsymbol{k}) + \eta_2\phi_2(\boldsymbol{k}). \tag{15}$$

This means that we may write the order parameter as follows:

$$\Delta(\boldsymbol{k}) = \eta_1[F_I(\boldsymbol{k})k_zk_x + F_{II}(\boldsymbol{k})k_zk_x^3] + \eta_2[F_I(\boldsymbol{k})k_zk_y + F_{II}(\boldsymbol{k})k_zk_y^3] \tag{16}$$

where F_I and F_{II} are invariant under all point group operations.

The forms of the functions F_I and F_{II} are determined by the details of the pairing interaction, and are set by physics at relatively high energies. In contrast to this, the complex coefficients η_j can be varied more easily, and can in fact vary with position when the superconductor is inhomogeneous. Thus, for an inhomogeneous superconductor the expansion (12) is generalized to the following:

$$\Delta(\boldsymbol{k}, \boldsymbol{R}) = \sum_{\mu j} \eta_{\mu j}(\boldsymbol{R})\phi_{\mu j}(\boldsymbol{k}). \tag{17}$$

An important point concerning time-reversal symmetry is also addressed by Yip and Garg [17]. They show that the basis functions $\phi_{\mu i}$ can always be chosen to be real. Thus, if Δ is given by (12), the time-reversed state is given by

$$\Delta^*(\boldsymbol{k}) = \sum_{\mu j} \eta^*_{\mu j}\phi_{\mu j}(\boldsymbol{k}). \tag{18}$$

The question of whether or not the order parameter breaks time-reversal invariance can be settled by examining the η's.

The discussion of this section is generalized in a straightforward way to triplet states. The vector $\boldsymbol{d}(\boldsymbol{k})$ should be expanded as follows:

$$\boldsymbol{d}(\boldsymbol{k}) = \sum_{\mu i} \boldsymbol{\eta}_{\mu i}\phi_{\mu i}(\boldsymbol{k}) \tag{19}$$

where the $\phi_{\mu i}$ are again basis functions as defined previously, but with vector coefficients. Thus, for each ℓ-dimensional representation, we have 3ℓ complex coefficients.

When spin–orbit coupling is strong, for the triplet case we need irreducible representations of G, not of $SO(3) \times G$. Then we may write

$$\boldsymbol{d}(\boldsymbol{k}) = \sum_{\mu i} \eta_{\mu i}\boldsymbol{\Phi}_{\mu i}(\boldsymbol{k}) \tag{20}$$

where the vector functions $\boldsymbol{\Phi}_{\mu i}$ form an irreducible representation of G.

3. Ginzburg–Landau theory

3.1. General remarks

One of the great virtues of the GL approach is that it allows us to construct a theory of the superconducting state with very few assumptions as to the microscopic details of the material. We start with the expansion of the order parameter in terms of the basis functions $\phi_{\mu j}$, and expand f, the free-energy density difference between the normal and the superconducting states, as a power series in the coefficients η [15, 18]. At a continuous

transition the η's should be small near T_c, and so the theory is meant to be valid at temperatures close to T_c. The GL theory is a mean-field theory and so does not include critical fluctuation effects, although it can be generalized to do so [15].

The important general principle is that all of the terms in f must be invariant under all of the operations of $\mathcal{G}$, the group introduced in the previous section. The leading terms that we can construct are then second order in the η's. Group theory tells us that the only quadratic invariants for a spatially uniform order parameter are (we consider here the case of weak spin–orbit coupling)

$$f_2 = \sum_\mu \alpha_\mu^s(T) \sum_i \eta_{\mu i}\eta_{\mu i}^* + \sum_\mu \alpha_\mu^t(T) \sum_i \boldsymbol{\eta}_{\mu i} \cdot \boldsymbol{\eta}_{\mu i}^*. \tag{21}$$

The first set of terms corresponds to singlet order parameters, while the second set corresponds to triplet order parameters. Microscopic theory is needed to compute the temperature dependent coefficients $\alpha(T)$; at the GL level of theory, we assume a certain general scenario for their behaviour.

At high temperatures all of the α's are positive, so f is minimized by setting all of the η's equal to zero. As we lower the temperature, at a certain critical temperature, one particular α_μ, either singlet or triplet, goes through zero and becomes negative. It is then favourable for the corresponding $\eta_{\mu i}$'s to be nonzero. So, close enough to T_c the order parameter should be a linear combination of basis functions from one particular representation. As the temperature is lowered still further, other representations may be mixed in; if this happens the residual symmetry group H may or may not change. Note that if H does not change, the zeros of the order parameter enforced by the structure of H (discussed in section 2.2) do not change.

To complete the theory, we must add in the following types of terms.

- Invariants which are fourth order in the η's.
- Gradient terms which are second order in both the order parameter and in gradients. In these terms the gauge-invariant derivative $\boldsymbol{D}$ appears, given by

  $$\boldsymbol{D} = \boldsymbol{\nabla} + \frac{2\mathrm{i}e}{\hbar c}\boldsymbol{A}. \tag{22}$$

  Our convention is that e is a positive number, so the electron charge is $-e$.
- The magnetic field term, given by

  $$f_B = (1/8\pi)[(\boldsymbol{\nabla} \times \boldsymbol{A}) - \boldsymbol{H}]^2 \tag{23}$$

  where $\boldsymbol{A}$ is the vector potential and $\boldsymbol{H}$ is the applied magnetic field. This is the appropriate form if we are working at fixed $\boldsymbol{H}$, with $\boldsymbol{A}$ varying with no constraint to minimize the free energy.

When we have the full set of terms in f, the order parameter and magnetic field are determined by minimizing F, the integral of f, with respect to the order parameter and the vector potential:

$$\frac{\delta F}{\delta \eta^*} = 0 \tag{24}$$

$$\frac{\delta F}{\delta \boldsymbol{A}} = 0. \tag{25}$$

An important consequence of the second equation is the following. It leads to an equation of the form

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{A}) = (4\pi/c)\boldsymbol{J} \tag{26}$$

and so allows us to identify the supercurrent $\boldsymbol{J}$.

3.2. One-dimensional representations

In certain cases, the GL theory, even for an unconventional order parameter, assumes exactly the same form as for a conventional order parameter [15]. We can then use the well developed GL theory which has been studied for several decades. These cases include the following.

(i) Situations in which the order parameter is a spin singlet, and transforms according to a one-dimensional representation. We may then write

$$\Delta(\boldsymbol{k}, \boldsymbol{R}) = \eta(\boldsymbol{R})\phi(\boldsymbol{k}). \tag{27}$$

(ii) Situations in which we have strong spin–orbit coupling, and a triplet order parameter of the following form:

$$\boldsymbol{d}(\boldsymbol{k}, \boldsymbol{R}) = \eta(\boldsymbol{R})\boldsymbol{\Phi}(\boldsymbol{k}) \tag{28}$$

where $\boldsymbol{\Phi}$ is a (vector) one-dimensional representation.

Note that case (i) covers conventional singlet pairing, as well as the d-wave order parameter being considered for the high-T_c superconductors. This order parameter is of the following form [11]:

$$\Delta_d(\boldsymbol{k}, \boldsymbol{R}) = \eta(\boldsymbol{R})F(\boldsymbol{k})(k_x^2 - k_y^2) \tag{29}$$

where F has the full crystal symmetry.

It is worth stressing that even for the conventional case, in which $\phi(\boldsymbol{k})$ belongs to the identity representation, $\phi(\boldsymbol{k})$ can still have a complicated $\boldsymbol{k}$-dependence, changing sign (or phase) as a function of $\boldsymbol{k}$. Recent work, at the microscopic level, on such order parameters includes [19, 20].

For any order parameter of type (i) or (ii), then, the GL functional takes the form

$$f = \alpha|\eta|^2 + \beta|\eta|^4 + \frac{1}{2}K_{ij}D_i\eta D_j^*\eta^* + f_B \tag{30}$$

where $\alpha(T) = \alpha_0(T - T_c)/T_c$, and the other coefficients are evaluated at T_c. The details of $\phi(\boldsymbol{k})$ have dropped out, except for playing a role in the microscopic calculation of the coefficients. For example, if $\phi(\boldsymbol{k})$ is conventional, the tensor K_{ij} will have the full symmetry of the normal state. If ϕ is unconventional, this may not be true. We might mention that recent work [21–24] has shown that the GL and London theories of superconductors with anisotropic K_{ij}'s can yield some surprising results.

4. Multidimensional representations—GL theory

4.1. Introduction

When more than one basis function appears in the expansion of Δ, the GL theory becomes much more interesting. In order to illustrate the wide variety of new phenomena, we concentrate on one particular case, a case which has been studied intensively in the context of UPt_3 [6, 25].

Consider a hexagonal crystal, with point group D_{6h}, and with strong spin–orbit coupling. Suppose that the pairing occurs in the triplet E_{1u} irreducible representation. Then the order parameter can be written as follows:

$$\boldsymbol{d}(\boldsymbol{k}) = \eta_1(\boldsymbol{R})\boldsymbol{\Phi}_1(\boldsymbol{k}) + \eta_2(\boldsymbol{R})\boldsymbol{\Phi}_2(\boldsymbol{k}). \tag{31}$$

The vector basis functions can be analysed using the results of section (2.3). It turns out that under all the operations of D_{6h}, (η_1, η_2) transforms as a vector in the xy-plane; thus we can use a vector notation:

$$\boldsymbol{\eta} = (\eta_1, \eta_2) = (\eta_x, \eta_y). \tag{32}$$

The free-energy density contains the invariants that we can construct from $\boldsymbol{\eta}$:

$$\begin{aligned} f = {} & \alpha\boldsymbol{\eta}\cdot\boldsymbol{\eta}^* + \beta_1(\boldsymbol{\eta}\cdot\boldsymbol{\eta}^*)^2 + \beta_2|\boldsymbol{\eta}\cdot\boldsymbol{\eta}|^2 + K_1 D_i\eta_j D_i^*\eta_j^* + K_2 D_i\eta_i D_j^*\eta_j^* \\ & + K_3 D_i\eta_j D_j^*\eta_i^* + K_4 D_z\eta_i D_z^*\eta_i^* + f_B. \end{aligned} \tag{33}$$

The supercurrent is then given by

$$J_i = \frac{4e}{\hbar}\mathrm{Im}[K_1\eta_j D_i^*\eta_j^* + K_2\eta_i D_j^*\eta_j^* + K_3\eta_j D_j^*\eta_i^* + K_4\hat{\boldsymbol{z}}_i\eta_j D_z^*\eta_j^*]. \tag{34}$$

Several comments concerning this free energy are in order.

(i) In all of these terms, the implied sums on i and j are two dimensional.

(ii) Two independent fourth-order invariants can be constructed. Note that for a complex $\boldsymbol{\eta}$ we can have $\boldsymbol{\eta}\cdot\boldsymbol{\eta} = 0$ for a nonzero $\boldsymbol{\eta}$; a positive value for β_2 will tend to encourage this.

(iii) The gradient terms allow for a complicated interaction between the vector potential and the order parameter. Consequences of this will emerge in future sections.

(iv) Details of the basis functions do not appear at the GL level of description. The forms of the $\boldsymbol{\Phi}_i(\boldsymbol{k})$ will, however, affect the microscopic calculation of the coefficients.

(v) A free energy of the same form also works for the E_{1g}, E_{2g}, and E_{2u} representations [6].

In the succeeding subsections, we will describe some of the interesting phenomena which can occur in a superconductor described by this free energy. We will not review the issue of whether this particular free energy is the appropriate one for superconducting UPt_3. For discussions of the various approaches being tried for this problem, see [6, 26, 27].

4.2. Homogeneous phases

We start our overview by considering which order parameters minimize f in the absence of any spatial gradients or magnetic fields [6, 25]. We then must minimize the bulk free-energy density given by

$$f_{bulk} = \alpha(\boldsymbol{\eta}\cdot\boldsymbol{\eta}^*) + \beta_1(\boldsymbol{\eta}\cdot\boldsymbol{\eta}^*)^2 + \beta_2|\boldsymbol{\eta}\cdot\boldsymbol{\eta}|^2. \tag{35}$$

First, note that we must have $\beta_1 > 0$ and $\beta_{12} > 0$ for stability. (We will use the notational shorthand $\beta_{12} = \beta_1 + \beta_2$.) Then there are two possibilities.

For $\beta_2 < 0$, f_{bulk} is minimized by an order parameter of the form

$$\boldsymbol{\eta}_0 = \eta_0(1, 0) \qquad \text{with } \eta_0 = \left(\frac{|\alpha|}{2\beta_{12}}\right)^{1/2}. \tag{36}$$

In fact, f_{bulk} is left unchanged if we rotate $\boldsymbol{\eta}_0$ by any angle in the xy-plane, or if we multiply it by a phase factor. So, besides the usual phase degeneracy, we have an extra rotational degeneracy. Part of this extra degeneracy is accidental, in that for D_{6h} the free energy is not required to be invariant under this continuous family of rotations; if terms of sixth order in η are included in the free energy, then this extra degeneracy is broken, and a discrete subset of this family of order parameters minimizes the free energy [25].

If $\beta_2 > 0$, the equilibrium order parameter is quite different. We then minimize f_{bulk} by using an order parameter of the form

$$\boldsymbol{\eta}_0 = \eta_0(1, \pm \mathrm{i}) \qquad \text{with } \eta_0 = \left(\frac{|\alpha|}{4\beta_1}\right)^{1/2}. \tag{37}$$

For this state, the gauge and rotational symmetries are linked, since a rotation of the two components is equivalent to multiplying the order parameter by a phase factor. This state also breaks time-reversal symmetry; some consequences of this will be discussed in the next section.

4.3. Internal angular momentum

We will now discuss an issue which can be called 'internal angular momentum' of the Cooper pairs [1, 28]. To see what this means, consider the free-energy density f. If we integrate by parts on the gradient terms, we can rewrite f as follows:

$$f = \alpha\eta_i\eta_i^* + \beta_1(\eta_i\eta_i^*)^2 + \beta_2|\eta_i\eta_i|^2 + K_1 D_i\eta_j D_i^*\eta_j^* + \frac{1}{2}K_{23}(D_i\eta_i D_j^*\eta_j^* + D_i\eta_j D_j^*\eta_i^*)$$
$$+ \frac{\mathrm{i}e}{\hbar c}(K_2 - K_3)(\boldsymbol{\eta}\times\boldsymbol{\eta}^*)\cdot\boldsymbol{B} + K_z D_z\eta_i D_z^*\eta_i^* + f_B. \tag{38}$$

Here, $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$ is the local magnetic field, and we use the notation $K_{23} = K_2 + K_3$. The gradient terms have been rearranged to include a term f_M, where

$$f_M = \frac{\mathrm{i}e}{\hbar c}(K_2 - K_3)(\boldsymbol{\eta}\times\boldsymbol{\eta}^*)\cdot\boldsymbol{B}. \tag{39}$$

This term has the form of a magnetic moment interacting with the magnetic field.

Another way to look at this idea is to examine the supercurrent. We can rearrange the terms in $\boldsymbol{J}$ to obtain the following expression:

$$J_i = \frac{4e}{\hbar}\mathrm{Im}\left[K_1\eta_j D_i^*\eta_j^* + \frac{1}{2}K_{23}(\eta_i D_j^*\eta_j^* + \eta_j D_j^*\eta_i^*) + K_4\hat{\boldsymbol{z}}_i\eta_j D_z^*\eta_j^*\right]$$
$$- \frac{\mathrm{i}e}{\hbar}(K_2 - K_3)[\boldsymbol{\nabla}\times(\boldsymbol{\eta}\times\boldsymbol{\eta}^*)]_i. \tag{40}$$

The last term, proportional to $\boldsymbol{\nabla}\times(\boldsymbol{\eta}\times\boldsymbol{\eta}^*)$, has a form analogous to the $\boldsymbol{\nabla}\times\boldsymbol{M}$ term in the current in electromagnetic theory.

One consequence of this term in $\boldsymbol{J}$ is the following. In the usual GL theory, discussed in section 3.2, there is a supercurrent if the phase of the order parameter varies in space; however, there is no current if only the magnitude varies. Here, the situation is different. Consider an order parameter of the following form:

$$\boldsymbol{\eta}(\boldsymbol{R}) = \eta_0(\boldsymbol{R})\frac{1}{\sqrt{2}}(1, \mathrm{i}). \tag{41}$$

That is, we have an order parameter of fixed phase and orientation, with a spatially varying magnitude.

For this order parameter, the supercurrent does not necessarily vanish. It is given by

$$\boldsymbol{J} = \frac{e}{\hbar}(K_2 - K_3)(\hat{\boldsymbol{z}}\times\boldsymbol{\nabla}\eta_0^2). \tag{42}$$

Thus, if the coefficient $K_2 - K_3$ is not zero, in many ways the superfluid behaves as if it has an internal angular momentum. We will later discuss microscopic calculations of this coefficient.

4.4. Calculation of H_{c2}

To compute the upper critical field, H_{c2}, one proceeds as follows. Imagine that we apply a very large external magnetic field $\boldsymbol{H} = H\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}$ is a unit vector, so that $\boldsymbol{\eta} = 0$ minimizes the free energy. Then, at fixed T, we lower H until f can be reduced by a nonzero order parameter. The value of H at which f becomes unstable to the onset of superconductivity is called $H_{c2}(T, \hat{\boldsymbol{n}})$. In a type I superconductor this continuous transition is pre-empted: before H reaches H_{c2}, it becomes favourable for the system to make a first-order transition to the Meissner state.

To do the calculation, then, we need only the following part of the free-energy density, which is quadratic in the order parameter:

$$f_Q = \alpha\eta_i\eta_i^* + K_1 D_i\eta_j D_i^*\eta_j^* + K_2 D_i\eta_i D_j^*\eta_j^* + K_3 D_i\eta_j D_j^*\eta_i^* + K_4 D_z\eta_i D_z^*\eta_i^*. \tag{43}$$

Furthermore, in the operator $\boldsymbol{D}$ we use the external vector potential $\boldsymbol{A}_{ex}$, such that $\boldsymbol{\nabla} \times \boldsymbol{A}_{ex} = \boldsymbol{H}$. Screening effects are of higher order in the order parameter, and may be ignored. Note also that the parameters β_1 and β_2 play no role in determining either the value of H_{c2} or the form of the order parameter right at H_{c2}; these parameters will play a role in determining the best way to combine degenerate order parameters below H_{c2} to form the vortex state. So, for a fixed value of $\alpha(T)$ and for fixed orientation $\hat{\boldsymbol{n}}$ we need to find the largest H at which a nonzero order parameter can make $f_Q = 0$. Since the free energy is a quadratic form in $\boldsymbol{\eta}$, we can solve this by turning it into an eigenvalue problem.

For specificity, we consider here only the case where $\hat{\boldsymbol{n}} = \hat{\boldsymbol{z}}$. The answer for H_{c2} is then surprisingly complex [29, 30]. We have two separate cases, depending on the values of the coefficients in the free energy.

(i) When

$$(K_2 - K_3)(2K_1 + K_{23}) > K_{23}^2 \tag{44}$$

we have

$$H_{c2} = \frac{\hbar c|\alpha|}{2eK_{13}} \tag{45}$$

and an order parameter given by

$$\boldsymbol{\eta} = (1, -\mathrm{i})L_0(x, y). \tag{46}$$

Here, $L_n(x, y)$ is the nth Landau level wavefunction for a particle in a magnetic field. For any given n there is a degenerate set of such wavefunctions; in addition, it should be noted that their particular form depends upon the gauge choice for $\boldsymbol{A}_{ex}$.

(ii) When the inequality goes the other way:

$$(K_2 - K_3)(2K_1 + K_{23}) < K_{23}^2 \tag{47}$$

we then have

$$H_{c2} = \frac{\hbar c|\alpha|}{2e\lambda} \tag{48}$$

$$\lambda = 3\left(K_1 + \frac{1}{2}K_{23}\right) - \left[2K_{23}^2 + \left(2K_1 + \frac{3}{2}K_3 + \frac{1}{2}K_2\right)^2\right]^{1/2}. \tag{49}$$

The order parameter is given by

$$\boldsymbol{\eta} = (1, \mathrm{i})L_0(x, y) + \omega(1, -\mathrm{i})L_2(x, y). \tag{50}$$

Case (i) is similar to the usual result for a conventional superconductor, in that it involves the lowest Landau level $L_0(x, y)$; case (ii) involves an intricate combination of L_0 and L_2.

In both cases there is a high degree of degeneracy. Just below H_{c2} we must construct an energy-minimizing linear combination of these functions to obtain the vortex state. For discussion of this, see [25].

4.5. Instability of the homogeneous state

We will now discuss an unusual scenario generated by the free energy (33), if the coefficients are in a certain range [1, 31, 32]. The basic question that we consider is the following. In the absence of an applied magnetic field, does a spatially uniform order parameter of the type considered in section (4.2) really minimize the free energy?

We start by considering the following related issue: what are the allowed values for the coefficients in the free energy $K_1, K_2, K_3, K_4, \alpha, \beta_1, \beta_2$? That is, in the absence of a microscopic calculation, can we use any general physical principles to put restrictions on these parameters? One such principle that we will use is that the free energy f should be bounded below. We have already noted that this means that we must have $\beta_1 > 0, \beta_{12} > 0$. It is easy to see, by considering situations in which $\boldsymbol{A} = 0$, that we must also have the following:

$$K_1 > 0 \qquad K_4 > 0 \qquad K_{123} > 0. \tag{51}$$

Whether these conditions are sufficient, as well as necessary, seems to be an open question at present. Allowing for the presence of a nonzero vector potential in the gradient terms makes any further progress in these arguments quite difficult.

Suppose now that $\beta_2 < 0$, and $\boldsymbol{H} = 0$, so that the order parameter that we will test for stability is given by

$$\boldsymbol{\eta}_0 = \eta_0(1, 0) \qquad \text{with } \eta_0^2 = \frac{|\alpha|}{2\beta_{12}} \tag{52}$$

up to a rotation or multiplication by a phase factor. Let us analyse the stability of this state. We can write

$$\boldsymbol{\eta} = \boldsymbol{\eta}_0 + \delta\boldsymbol{\eta}(\boldsymbol{R}) \tag{53}$$

$$\boldsymbol{A} = \boldsymbol{A}_0 + \delta\boldsymbol{A}(\boldsymbol{R}) = \delta\boldsymbol{A}(\boldsymbol{R}) \tag{54}$$

$$f = f_0 + \delta f. \tag{55}$$

Note that f_0 is evaluated using $\boldsymbol{\eta}_0$ and $\boldsymbol{A}_0 = 0$, and that δf will have no terms linear in $\delta\boldsymbol{\eta}$ or $\delta\boldsymbol{A}$; in δf we keep the second-order terms. Thus δf is a quadratic form in $\delta\boldsymbol{\eta}, \delta\boldsymbol{A}$.

When we analyse this quadratic form we find, as expected, that it has several zero eigenvalues, corresponding to rotations and gauge transformations. The key question, then, is that of whether δf has any negative eigenvalues; if it does, then the order parameter (52) is not the lowest energy state. The surprising answer is that, if the coefficients are in a certain range, which does not seem to be forbidden on any *a priori* grounds, then there are indeed negative eigenvalues.

There are two cases to consider, depending on the sign of the quantity

$$\gamma = K_{23}\left[\frac{|\beta_2|}{2\pi} - \frac{4e^2}{\overline{h}^2c^2}K_{13}^2\right].$$

(i) If $\gamma < 0$, then negative eigenvalues appear if the following condition is met:

$$K_3^2 > \left[K_1 + \frac{\overline{h}c}{2e}\left(\frac{|\beta_2|}{2\pi}\right)^{1/2}\right]^2. \tag{56}$$

(ii) If $\gamma > 0$, then negative eigenvalues appear if the following holds:

$$K_2^2 > \left[K_{123} + \frac{\hbar c}{2e} \left(\frac{|\beta_2|}{2\pi} \right)^{1/2} \right]^2. \tag{57}$$

The corresponding eigenvectors have both $\delta\boldsymbol{\eta}$ and $\delta\boldsymbol{A}$ nonzero. In a sense what happens is that the order parameter distorts, a supercurrent is generated, and a magnetic field is thus produced; this field interacts with the order parameter and achieves a lowering of the free energy. With no applied field, the superconductor creates its own $\boldsymbol{B}(\boldsymbol{R})$. The gradient terms contribute a net negative total to the free energy.

The preceding stability analysis does not allow one to study the ultimate equilibrium state. This has been done by using numerical relaxation techniques, and we refer the reader to the literature [32] to see pictures of the new equilibrium state. One point that emerges from the numerical work is that f appears to be bounded below, for parameters chosen to allow the instability. It also turns out, in a related phenomenon, that a magnetic field can actually raise the transition temperature [33].

4.6. Structure of a single vortex

We now turn to the study of a single isolated vortex line; the energy per unit length of this entity is the key input to computing H_{c1}. More importantly, a surprisingly rich structure is sometimes predicted for the order parameter's spatial dependence, leading in some cases to an unexpected symmetry breaking. We review one particular case which has been treated in the literature [34, 35, 25]. Assume that $\beta_2 > 0$, and that the order parameter has the form $\boldsymbol{\eta} = (1, \mathrm{i})\eta_0$ in the absence of the vortex line. We now put in a vortex line parallel to the $\hat{\boldsymbol{z}}$-axis, centred on the line $x = 0,\ y = 0$. We will consider two separate cases: vortices with clockwise and with anticlockwise flows. These two cases are quite different, since the $(1, \mathrm{i})$ state breaks time-reversal invariance.

Defining $\boldsymbol{r} = x\hat{\boldsymbol{x}} + y\hat{\boldsymbol{y}}$, we then have at large r,

$$\boldsymbol{\eta}(\boldsymbol{r}) = \exp(\pm \mathrm{i}\theta)\eta_0 \chi(r)(1, \mathrm{i}). \tag{58}$$

Here, θ is the polar angle in the xy-plane and $\chi(r)$ is a cylindrically symmetric function which approaches unity at large r; the superfluid density tensor is isotropic in the xy-plane for the $(1, \mathrm{i})$ state, so the phase of the order parameter is simply $\pm\theta$ at large distances from the vortex axis. So, at large r we simply have the bulk order parameter multiplied by $\exp(\pm \mathrm{i}\theta)$. The question is, what happens to the order parameter as r decreases? Here are the results.

(i) The $\exp(+\mathrm{i}\theta)$ vortex—for a range of parameters, the order parameter keeps the cylindrically symmetric form (58) for all r; large values of β_2/β_1 tend to favour this. However, for other ranges of coefficients, at smaller values of r a complicated order parameter structure develops which breaks the cylindrical symmetry. Instead, the core region has a triangular pattern.

(ii) The $\exp(-\mathrm{i}\theta)$ vortex—for a certain range of parameters the order parameter keeps the cylindrically symmetric form. But, for other coefficient choices, the core region is not cylindrically symmetric, and adopts a crescent-shaped pattern.

We refer the reader to the literature for interesting pictures of these broken-symmetry core regions [34]. Note that because of the $\exp(\pm \mathrm{i}\theta)$ factor, η_x and η_y must each vanish at some point. However, they need not vanish at the same point, and so in some cases the quantity $|\boldsymbol{\eta}|^2$ is never zero for the vortex line. One other point which should be stressed

is that, if the superconductor is in the $(1, \mathrm{i})$ state, the value of H_{c1} will in general be different for $\boldsymbol{H} \parallel \hat{\boldsymbol{z}}$ and for $\boldsymbol{H} \parallel -\hat{\boldsymbol{z}}$. This is because the two vortex cases discussed in this section will in general have different line energies. The value of the coefficient $K_2 - K_3$, already discussed in the context of the intrinsic angular momentum, plays a key role in these considerations [34].

5. Superconducting Fermi liquid theory

5.1. Introduction

The Ginzburg–Landau theory that we have been discussing is quite general, relying only on very basic assumptions concerning the correlations present in the superconducting state. However, there are a wide range of phenomena about which the GL theory is silent; these phenomena require a more microscopic theory for their description. Even concerning GL theory itself, we need a more microscopic theory to calculate the various coefficients which arise, and to determine the range of validity of the GL description. For example, one could ask: what is the shortest length scale at which the GL theory is valid?

A more microscopic theory also allows us to gain insight into the significance of the $\boldsymbol{k}$-dependence of $\Delta_{\alpha\beta}(\boldsymbol{k})$. Recall that in the GL theory only the expansion coefficients η_i play an explicit role. In this section we will see that various features of the order parameter's $\boldsymbol{k}$-dependence are particularly important. Such features include whether the order parameter vanishes at points in $\boldsymbol{k}$-space, and whether it changes sign, or more generally its phase, as $\boldsymbol{k}$ varies.

The trade-off is that a more powerful microscopic theory will usually be less general than the GL approach. To develop such a theory, in the absence of a complete first-principles solution, we must make a set of definite assumptions concerning the nature of the material; such assumptions can of course then be tested by experiment. In this section we will review the most fully developed such microscopic theory, the theory of a superconducting Fermi liquid (SFL). This theory is essentially the original BCS theory, generalized to unconventional order parameters and to arbitrary pairing mechanisms, presented with its modern justification.

We should stress that the SFL theory is itself not the most microscopic approach. It can only be justified by, and contains parameters which can only be calculated by, a more fundamental theory. This will become clear as our exposition proceeds.

We refer the reader to the literature for a complete discussion of the SFL theory [18, 36–38]. Here, we briefly note that the essential idea is that at low temperatures the normal state is taken to be a Landau Fermi liquid, in which the important excitations are long-lived electronic quasiparticles which carry spin $\frac{1}{2}$ and charge $-e$. These are the usual Bloch electrons of the normal state, given a sophisticated interpretation. It is assumed that there is a well defined Fermi surface, which may have several disconnected pieces, and that there is a characteristic normal-state energy scale called the Fermi energy E_F. Finally, it is necessary that $T_c \ll E_F$; physically, this means that the onset of superconductivity does not significantly perturb the inner structure of the quasiparticles.

In the rest of this section we will review several illustrative applications of the SFL theory. For clarity, we must establish our notation. The important point then is that in the SFL, all of the action happens in the vicinity of the Fermi surface. We therefore label a given point on this surface in $\boldsymbol{k}$-space with a two-dimensional variable s. For example, in this theory only the value of the order parameter near the Fermi surface plays a role, so we write $\Delta_{\alpha\beta}(s)$. When the Fermi surface is a sphere or a circle, it can be convenient to use

$\hat{\boldsymbol{k}}$ to label Fermi surface points.

The Fermi surface integral of a function $F(s)$, denoted by $\langle F \rangle$, is given by

$$\langle F \rangle = \int_{FS} \mathrm{d}^2 s \; n(s) F(s). \tag{59}$$

Here, $n(s)$ is the differential density of states at s, normalized to one:

$$\int_{FS} \mathrm{d}^2 s \; n(s) = 1. \tag{60}$$

This integral is over the entire Fermi surface, including all disconnected pieces. We denote the Fermi velocity at s by $\boldsymbol{v}_F(s)$, and the total density of states at the Fermi surface for one spin population by $N(0)$. For simplicity, we will not include in what follows the Landau quasiparticle interaction terms [36].

The most useful way to formulate the theory of the SFL is to use thermodynamic Green's functions, and a version of the Gorkov equations. Such a formulation makes it straightforward to include impurity scattering, and to treat spatially inhomogeneous and time-dependent situations. One particularly nice approach is the so-called quasiclassical theory which takes advantage of the basic physical assumptions concerning the SFL to achieve a simplification of the equations [18, 39–41].

Before proceeding, we should address the question of length scales. The basic, temperature-independent coherence length, ξ_0, is given by

$$\xi_0 \sim \frac{\hbar v_F}{T_c}. \tag{61}$$

The GL theory is valid on length scales greater than ξ_0; this limit emerges from the derivation of the GL theory from the SFL theory [42]. The SFL approach can handle length scales shorter than ξ_0, but is restricted to scales greater than the basic microscopic length of order $1/k_F$.

To illustrate the connection to the GL theory, we quote one set of results [41, 43]. For a spin-singlet order parameter, belonging to a one-dimensional irreducible representation, we show the SFL-derived formulae for the coefficients in the GL free energy (30), in the absence of impurity scattering:

$$\alpha = N(0)\frac{T - T_c}{T_c} \tag{62}$$

$$\beta = \frac{7\zeta(3)N(0)}{16(\pi T_c)^2}\langle |\phi|^4 \rangle \tag{63}$$

$$K_{ij} = \frac{7\zeta(3)N(0)\hbar^2}{8(\pi T_c)^2}\langle v_{Fi} v_{Fj} |\phi|^2 \rangle. \tag{64}$$

Here, $\phi(s)$ is the properly normalized ($\langle |\phi|^2 \rangle = 1$) basis function.

5.2. The gap equation

As an important example, we consider the gap equation for a spin-singlet order parameter. This will allow us to see how the group theoretical basis functions, which we have discussed earlier, emerge from a more microscopic approach. In the SFL theory, $\Delta(s)$ plays the role of an off-diagonal (in particle–hole space) self-energy. It is temperature dependent and

vanishes at T_c. It is determined, for a spatially homogeneous situation in the absence of impurities, by the following equation [40]:

$$\Delta(s) = N(0)\pi T \sum_{|\epsilon|<E_c} \int_{FS} \mathrm{d}^2 s' \; n(s') \frac{V(s,s')\Delta(s')}{[\epsilon_n^2 + |\Delta(s')|^2]^{1/2}}. \tag{65}$$

We have introduced the temperature-dependent Matsubara frequencies, given by $\epsilon_n = (2n+1)\pi T$, where n is an integer [42]. The sum over ϵ_n has a cut-off E_c, so that $|\epsilon_n| < E_c$; this cut-off should satisfy the following inequality: $T_c \ll E_c \ll E_F$. We will say more about this cut-off later.

The pairing potential $V(s,s')$ contains all the complicated interactions which go into the off-diagonal self-energy [41]. An actual calculation of this quantity would require a more fundamental theory. However, we can further analyse this effective potential as follows. The pairing potential must have the symmetry of the normal state. Thus, for any operation $\mathcal{R}$ of the point group we must have

$$V(\mathcal{R}s, \mathcal{R}s') = V(s,s'). \tag{66}$$

Group theory then tells us that we can expand $V(s,s')$ in terms of basis functions as follows:

$$V(s,s') = \sum_{\mu} V_\mu \sum_j \phi_{\mu j}(s)\phi^*_{\mu j}(s') \tag{67}$$

where $\phi_{\mu j}(s)$ is a basis function for the irreducible representation μ. Note that each irreducible representation may occur more than once in the sum.

The critical temperature T_c will be the highest temperature at which the gap equation has a nonzero solution. To find T_c we use the fact that the order parameter goes to zero at the transition temperature; we can linearize the right-hand side of (65), and then expand the order parameter in terms of the basis functions:

$$\Delta(s) = \sum_{\mu j} \Delta_{\mu j}\phi_{\mu j}(s). \tag{68}$$

We also use the orthonormality of the basis functions:

$$\int_{FS} \mathrm{d}^2 s \; n(s)\phi^*_{\mu i}(s)\phi_{\nu j}(s) = \delta_{ij}\delta_{\mu\nu}. \tag{69}$$

We then get a separate T_c for each representation. The physical transition temperature will be the highest one, say for ν, and we then have

$$T_c = 1.13 E_c \exp\left(\frac{-1}{N(0)|V_\nu|}\right). \tag{70}$$

This is the usual BCS result, generalized to an arbitrary representation. Within the SFL theory, the somewhat arbitrary parameters E_c and V_ν should disappear when computing any other physical quantities. The correct procedure when doing theory at this level is to eliminate these two parameters in favour of the measured T_c, using this equation. Thus, this equation should not be viewed as a prediction of the transition temperature; rather, it serves to eliminate the two unwanted parameters and replace them by a physical quantity.

At temperatures below T_c, we must treat the full nonlinear gap equation. The nonlinear terms will have several effects. For a multidimensional representation, they will select the proper linear combination of basis functions which make up the order parameter. The nonlinear terms can also lead to other representations being mixed in with the one that occurs right at T_c. One other point should be noted; since it is a nonlinear equation, the gap equation may have several inequivalent solutions (i.e. solutions not related by a symmetry

operation) at a given temperature. The proper solution will then be the one with the lowest free energy. For discussion on how to compute the free energy, see [41].

One important property of the basis functions should be stressed at this point; except for the identity representation, the Fermi surface average of $\phi_{\mu j}(s)$ is zero:

$$\int_{FS} \mathrm{d}^2 s \; n(s)\phi_{\mu j}(s) = 0 \qquad \text{for } \mu \neq \text{identity representation.} \tag{71}$$

This means that $\phi_{\mu j}(s)$ must have a nontrivial s-dependence, changing sign or phase in such a way that the average vanishes.

5.3. The density of states

An important feature of the superconducting phase is that the number of low-energy states available to the system, which is reflected in the density of states $N_s(E)$, can be greatly reduced. This need not always happen, as the case of gapless superconductivity shows [44, 45]. The density of states has a great influence on many other quantities, such as the superfluid density and the specific heat, and is itself an important experimental property. (For discussion of the superfluid density, see [43, 46–49].) In this section we will review the basic theory of $N_s(E)$ for a pure system. In the next section we will discuss the effects of impurity scattering on this quantity. When the order parameter is unconventional, impurity scattering can have dramatic effects on the density of states. Our discussions of $N_s(E)$ will serve as an example of the role played by the $\boldsymbol{k}$-dependence of the order parameter.

To compute the density of states, we first note that in the normal state we have well defined single-particle states in the vicinity of the Fermi surface, with energies $\epsilon(\boldsymbol{k})$, where

$$\boldsymbol{v}_F(s) = \frac{1}{\hbar}(\boldsymbol{\nabla}_k \epsilon)_{k=k_F}. \tag{72}$$

We will measure $\epsilon(\boldsymbol{k})$ relative to E_F, so that $\epsilon(s) = 0$. Then, for a spin-singlet order parameter, the elementary excitations in the superconducting state have doubly degenerate energies $E(\boldsymbol{k})$ given by

$$E^2(\boldsymbol{k}) = \epsilon^2(\boldsymbol{k}) + |\Delta(s)|^2. \tag{73}$$

Here, s is the point on the Fermi surface in the direction of $\boldsymbol{k}$. The density of states is then given by

$$N_s(E) = \int \frac{\mathrm{d}^3 k}{4\pi^3} \; \delta(E - E(\boldsymbol{k})) = 2N(0)E \int_{FS} \mathrm{d}^2 s \; n(s) \frac{\Theta(E - |\Delta(s)|)}{[E^2 - |\Delta(s)|^2]^{1/2}}. \tag{74}$$

Note that we have written the density of states in terms of a Fermi surface integral, and that the step function $\Theta(x)$ restricts the integral to the parts of the Fermi surface where $E > |\Delta(s)|$. We can also see that $N_s(E)$ depends only on the magnitude of the order parameter, $|\Delta(s)|$; when impurity scattering is present, this is no longer true.

Using this equation, we can consider several exemplary cases [2].

- Suppose that over the entire Fermi surface, the order parameter is constant, so that $|\Delta(s)| = \Delta_0$; then, $N_s(E) = 0$ for $E < \Delta_0$. We have

$$N_s(E) = 2N(0) \frac{E}{[E^2 - \Delta_0^2]^{1/2}} \Theta(E - \Delta_0). \tag{75}$$

- Suppose that $\Delta(s)$ vanishes at isolated points on the Fermi surface, and does so linearly. For example, imagine that some piece of the Fermi surface can be parametrized by spherical coordinates θ and ϕ, and that the order parameter behaves as $|\Delta| = \Delta_0 \sin(\theta)$ near the point $\theta = 0$. Then at small energies we have $N_s(E) \sim E^2$.

- Another possibility is that the order parameter vanishes at lines on the Fermi surface. If, for example, we can parametrize a piece of the Fermi surface by spherical coordinates θ and ϕ, and $\Delta(s) = \Delta_0 \cos(\theta)$ near the line $\theta = \pi/2$, then we have $N_s(E) \sim E$ at small energies.
- An interesting result can be found for a gap of the form $\Delta(s) = \Delta_0 \sin^2(\theta)\cos(2\phi)$, for a spherical Fermi surface. At low energies the density of states acquires a logarithmic correction: $N_s(E) \sim E|\ln(E)|$ [50].

Up to now, we have been treating $E(\boldsymbol{k})$ for a singlet order parameter. For triplet superconductors, the spin structure of the order parameter adds an extra complication. For a given $\boldsymbol{k}$, we have two excitations which are not necessarily degenerate. In terms of the $\boldsymbol{d}$-vector notation, we then get [2]

$$E_{\pm}^2(\boldsymbol{k}) = \epsilon^2(\boldsymbol{k}) + |\boldsymbol{d}(s)\cdot\boldsymbol{d}^*(s)| \pm |\boldsymbol{d}(s)\times\boldsymbol{d}^*(s)|. \tag{76}$$

For unitary states, defined as those for which $\boldsymbol{d}(s)\times\boldsymbol{d}^*(s) = 0$, we have a doubly degenerate spectrum, just as in the singlet case. For nonunitary order parameters, this degeneracy is broken. For a simple example of how this works, consider an order parameter of the following form:

$$\boldsymbol{d}(s) = -\frac{(\hat{\boldsymbol{x}} + \mathrm{i}\hat{\boldsymbol{y}})}{2}\Delta_0(s). \tag{77}$$

This corresponds to an order parameter with $\Delta_{\uparrow\uparrow} = \Delta_0(s)$, and all other components equal to zero. Our formula then gives $E_+^2 = \epsilon^2 + |\Delta_0|^2$, $E_-^2 = \epsilon^2$. This result is easy to interpret; the up spins have an energy gap, and the down spins do not. For more discussion of this type of order parameter, see [51].

5.4. Impurity scattering

Scattering by ordinary nonmagnetic impurities can have many dramatic effects when the superconducting order parameter has a strong $\boldsymbol{k}$-dependence [52, 53]. Recall that, in the absence of impurities, the density of states depends only on $|\Delta(s)|$, and that this dependence is quite simple to understand in terms of the spectrum $E(\boldsymbol{k})$. Once impurity scattering is introduced, the situation becomes much more interesting. $N_s(E)$ can now depend strongly on the $\boldsymbol{k}$-dependent phase of the order parameter, as well as on its magnitude. The order parameter no longer has a straightforward interpretation as an energy gap.

Here, we will briefly review this topic, without going into the technical details. Within the SFL theory, impurity scattering is treated as follows [40, 41]. The superconductor contains a density c of impurities, which are randomly distributed. Each impurity has a potential $v(s, s')$, which gives the amplitude for scattering of a quasiparticle from s to s' on the Fermi surface. For simplicity, theorists often take this potential to be of s-wave form, meaning $v(s, s') = v$; we will do so here.

Then, in the normal state the mean time between collisions τ is given by

$$\frac{\hbar}{2\tau} = \frac{cN(0)\pi v^2}{1 + (N(0)\pi v)^2}. \tag{78}$$

In the normal state, and for isotropic superconductors (i.e., those with $\Delta(s) = \Delta_0$), physical properties usually depend only on τ, and not on the separate values of c and v. In the case of unconventional superconductors this no longer holds [54]. It is thus convenient to define another parameter σ as follows [55]:

$$\sigma = \frac{(N(0)\pi v)^2}{1 + (N(0)\pi v)^2}. \tag{79}$$

This parameter measures the strength of the potential of a single impurity. The Born limit (weak potential) corresponds to $\sigma \to 0$, while the unitarity limit (strong scattering) corresponds to $\sigma \to 1$. One important term should also be introduced at this point. We say that a superconductor is 'gapless' if $N_s(E = 0) > 0$, that is, if the density of states at zero energy is not zero. A gapless superconductor, then, shares one key characteristic of a normal Fermi liquid, namely a macroscopic value for $N_s(E = 0)$. Note that the two cases discussed in the last section, with $N_s(E) \sim E$ and $N_s(E) \sim E^2$ at low energies, are not gapless according to this definition.

Having introduced the appropriate terminology, we can now discuss some of the effects of impurity scattering on the density of states, the transition temperature, and the GL coefficients.

To illustrate the density-of-states effects, we will quote some results for a specific case [56], which has received much theoretical attention in the context of the high-T_c superconductors. We consider a two-dimensional metal, with a circular Fermi surface, in which the gap has point nodes. (This is analogous to line nodes for a three-dimensional system.) We take an order parameter of the form

$$\Delta(\hat{\boldsymbol{k}}) = \Delta_0(\hat{\boldsymbol{k}}_x^2 - \hat{\boldsymbol{k}}_y^2). \tag{80}$$

Then, with no impurities, $N_s(E) \sim E$ at low energies. When $\sigma = 1$, the density of states at $E = 0$, for a low concentration of impurities, is given by

$$N_s(E = 0) = \frac{4N(0)\gamma}{\pi\Delta_0} \ln\left(\frac{4\Delta_0}{\gamma}\right) \tag{81}$$

where γ is a new energy scale introduced by impurity scattering in the unitarity limit. It is determined by solving the implicit equation

$$\gamma^2 \ln\left(\frac{4\Delta_0}{\gamma}\right) = \frac{\pi\hbar\Delta_0}{4\tau}. \tag{82}$$

In the Born limit ($\sigma \to 0$), for small concentrations of impurities, the density of states at $E = 0$ is given by

$$N_s(E = 0) = 16N(0)\frac{\tau\Delta_0}{\hbar} \exp\left(-\frac{\pi\tau\Delta_0}{\hbar}\right) \tag{83}$$

For small concentrations, such that $\tau\Delta_0/\hbar \gg 1$, this Born limit answer, although not zero, can be very small indeed.

The question arises of what are the crucial aspects of the form of the order parameter which lead to these sometimes large impurity effects on the density of states. The order parameter given by (80) has two key features: (I) its Fermi surface average vanishes, reflecting the fact that the order parameter changes sign; (II) it goes to zero at points on the Fermi surface. Recent work has shed light on this question by considering a family of order parameters which have feature (I), but not feature (II) [55, 57]. This work shows that many of the impurity effects are still present, even in the absence of nodes. Thus the vanishing Fermi surface average plays a key role in enhancing the effects of impurity scattering.

We now review the effects of impurity scattering on the transition temperature. It turns out that for s-wave impurities (recall, this means that we take $v(s, s') = v$), a very general and universal answer emerges. Our discussion of the gap equation showed that at T_c, the order parameter belongs to one particular irreducible representation. For any nonidentity representation, the transition temperature is lowered by the presence of impurities; the equation determining T_c is given by [1, 53]

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\hbar}{4\pi\tau T_c}\right). \tag{84}$$

Here, T_{c0} is the transition temperature in the absence of impurity scattering, and $\psi(x)$ is the digamma function. This formula, for the T_c-reduction from nonmagnetic impurities, is exactly the same as the formula for the T_c-reduction in an isotropic superconductor from magnetic impurities [44], if the magnetic impurities are treated classically (i.e. if the Kondo effect is not taken into account).

We conclude this section by discussing the coefficient $K_2 - K_3$, which played an important role in the GL theory analysed in section 4. In turns out that, in the framework of the SFL theory, $K_2 - K_3$ is equal to zero in the absence of impurity scattering [1]. There are two ways to try to get a nonzero value for this coefficient. One way is to add in impurity scattering. The other way is to go beyond the approximations inherent in the SFL theory; this is sometimes known as putting in strong-coupling effects. The effects of impurity scattering on $K_2 - K_3$ have been addressed in several papers [1, 28, 58]. One point that emerges from the calculations is that it can be necessary to go beyond the s-wave impurity model in order to get a nonzero answer.

5.5. Single-impurity calculations

In contrast to the results discussed in the previous section, we can also treat a single, isolated impurity immersed in a host superconductor. Many different aspects of the neighbourhood of such an impurity may be investigated. The SFL theory can describe this situation on length scales greater than $1/k_F$ [59–61]. As a particularly interesting example, we consider the following situation. Suppose that the superconducting order parameter is a complex function of $\boldsymbol{k}$, and so breaks time-reversal symmetry in its spatial coordinates. An example of this is the A-phase type of order parameter, familiar from superfluid ^{3}He, given by

$$\boldsymbol{d}(\boldsymbol{k}) = \hat{\boldsymbol{z}}\Delta_0(\hat{\boldsymbol{k}}_x + \mathrm{i}\hat{\boldsymbol{k}}_y). \tag{85}$$

The key point is that a pattern of supercurrents gets set up [59, 62], which is significant out to distances of order $\xi(T)$ from the impurity. One effect of these currents is to create a localized magnetic field. Thus, even a nonmagnetic impurity can lead to magnetic effects when the order parameter breaks time-reversal symmetry.

The SFL theory allows us to compute these supercurrents, $\boldsymbol{J}(\boldsymbol{R})$. Note that for a strongly type-II superconductor, the Meissner screening of these currents will be negligible. The magnetic field at the impurity site (taken to be $\boldsymbol{R} = 0$) is then given by

$$\boldsymbol{B}(0) = \frac{1}{c}\int \mathrm{d}^3R\ \frac{\boldsymbol{R}\times\boldsymbol{J}(\boldsymbol{R})}{R^3}. \tag{86}$$

Here c is the speed of light. An estimate for the size of this field is given by [62]

$$|\boldsymbol{B}| \approx a(T)(ek_F^2)\left(\frac{T_c}{T_F}\right)^2\left(\frac{v_F}{c}\right)(\sigma). \tag{87}$$

In this formula, $a(T)$ is dimensionless, vanishes at the critical temperature, and is of order one at lower temperatures. The quantity σ was introduced in the last section, and is a measure of the strength of the impurity potential. Note that the factor ek_F^2 has the dimensions of a magnetic field, and can be quite large. However, it is reduced by the small factors v_F/c and $(T_c/T_F)^2$.

We can also investigate the net magnetic moment due to these impurity currents. It is given by

$$\boldsymbol{M} = \frac{1}{2c}\int \mathrm{d}^3R\ \boldsymbol{R}\times\boldsymbol{J}(\boldsymbol{R}). \tag{88}$$

The surprising result is that, in a wide variety of cases, the current changes sign in such a way that we obtain $\boldsymbol{M} = 0$. This answer holds for any Fermi surface, order parameter, and impurity potential, if certain assumptions hold. For a discussion of this issue, see [59, 63].

6. Conclusion

We hope to have provided some idea of the range of new phenomena which can arise in a superconductor with an unconventional order parameter. Broadly speaking, these new phenomena are due to two features of such order parameters. At the GL level, order parameters requiring a multicomponent description lead to a more complex GL free-energy functional. Such a free energy, which involves an intricate coupling of the vector potential to the order parameter, leads to a number of perhaps surprising physical effects; section 4 presented a representative sample of these effects.

At the more microscopic level of the SFL description, it is the $\boldsymbol{k}$-dependence of the order parameter which is responsible for many new effects. The vanishing Fermi surface average of any order parameter belonging to a nonidentity representation ensures a complicated $\boldsymbol{k}$-dependence. Section 5 provided a brief survey of phenomena at the SFL level.

One challenging aspect to this rich range of possible behaviour is that an interesting experimental result can have many (perhaps too many!) different, mutually exclusive explanations. The discussion given by Rainer [64], concerning the SFL theory itself, makes a similar point. The joint efforts of theorists and experimentalists will be needed to satisfactorily prove that phenomena in real physical systems are due to particular unconventional order parameters.

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