The effect of impurities on Fulde-Ferrell-Larkin-Ovchinnikov superconductors

2001 J. Phys.: Condens. Matter 13 9259

(http://iopscience.iop.org/0953-8984/13/41/315)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 9259–9270 PII: S0953-8984(01)26634-X

The effect of impurities on Fulde–Ferrell–Larkin–Ovchinnikov superconductors

D F Agterberg[1,2] and Kun Yang[1]

[1] National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, FL 32306, USA
[2] Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, WI 53201, USA

Received 6 July 2001
Published 28 September 2001
Online at stacks.iop.org/JPhysCM/13/9259

Abstract

We derive the Ginzburg–Landau theory of unconventional singlet superconductors in the presence of a Zeeman field and impurities, in order to examine the resulting Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) phases. We show that the behaviour of the FFLO phases in unconventional superconductors in the presence of impurities is qualitatively different from that found for s-wave superconductors.

1. Introduction

In 1964 Fulde and Ferrell [1] and Larkin and Ovchinnikov [2] demonstrated that a superconducting state with an order parameter that oscillates spatially may be stabilized by a large applied magnetic field or an internal exchange field. Such a Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) state was subsequently shown to be readily destroyed by impurities [3] and has never been observed in conventional low-T_c superconductors. The question of observing an FFLO phase in an unconventional superconductor has only been addressed more recently. In particular organic, heavy-fermion, and high-T_c superconductors appear to be promising candidates for exhibiting such states [4–22]. These new classes of superconductors are believed to provide conditions that are favourable to the formation of FFLO states, because many of them are: (i) strongly type II superconductors, so the upper critical field H_{c2} can easily approach the Pauli paramagnetic limit; and (ii) layered compounds, so, when a magnetic field is applied parallel to the conducting plane, the orbital effect is minimal, and the Zeeman effect (which is the driving force for the formation of FFLO states) dominates the physics. Indeed, some experimental indications of the existence of the FFLO state have been reported [4, 11, 13, 19]. All of these materials have been argued to be unconventional superconductors and in this way differ from the case originally considered by Fulde, Ferrell, Larkin, and Ovchinnikov. Motivated by this possibility we have derived the Ginzburg–Landau (GL) free-energy functional for unconventional superconductors in the presence of Zeeman splitting and an impurity potential, and use it to study the possible FFLO phases. This is not a commonly used approach for examining the FFLO phase. To our knowledge it has previously only been discussed in the context of clean s-wave superconductors by Buzdin and Kachkachi [17]. However, as we show below, it represents a very powerful approach for studying the FFLO phase since the simplicity of the resulting theory allows complexities such as non-s-wave pairing, impurities, and even strong-coupling effects to be included (though this is not done here). The stability of the various superconducting phases and, to some degree, the topology of the superconducting phase diagram can be examined within this approach. These results help to clarify the nature of the FFLO phase and can also be used as a guide for a theory extended to all temperatures and magnetic fields.

Using a functional integral formalism, we derive the GL free-energy functional for single-component singlet superconductors in the presence of impurities and Zeeman fields in the weak-coupling limit. The resultant GL free energy is valid near the second-order normal-to-superconductor phase transition line in the (T, H) plane. This line will be denoted by $[T, H(T)]$. The resulting instability to the FFLO phase appears readily within this approach due to the change of sign of the gradient term $\kappa|\nabla\Psi|^2$ along the line $[T, H(T)]$. The point at which the coefficient κ changes sign (denoted as $[T^*, H(T^*)]$) is a tricritical point. At this point the normal, uniform superconducting, and FFLO phases all meet (see figure 1). An intriguing feature of the weak-coupling clean limit is that the fourth-order uniform term $\beta|\Psi|^4$ also changes sign at the tricritical point. It is this term that determines the form of the FFLO phase. In particular, for a given momentum $\boldsymbol{q}$ the two solutions $\Psi \sim e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ and $\Psi \sim e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}$ are degenerate superconducting states at the normal-to-superconductor instability. The fourth-order term breaks this degeneracy and selects either a $\cos(\boldsymbol{q}\cdot\boldsymbol{r})$ (LO phase) or an $e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ (FF phase) type of order parameter. Since the magnitude of the order parameter is spatially uniform for the FF phase and vanishes at lines in real space for an LO phase, a negative β stabilizes the LO phase. Note that the complete GL free energy in this case requires inclusion of terms of the form $|\Psi|^6$ and $|\Psi|^2|\nabla\Psi|^2$ to be bounded. These considerations have appeared in the work of Buzdin and Kachkachi [17] for conventional s-wave superconductors in the clean limit and are shown here to remain true for unconventional superconductors.

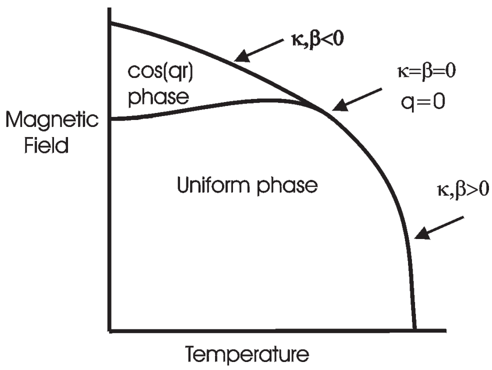

Figure 1. The qualitative phase diagram for clean superconductors. The $\cos\boldsymbol{q}\cdot\boldsymbol{r}$ form of the order parameter is only valid near the normal-to-FFLO transition line. The direction of $\boldsymbol{q}$ in the FFLO phase may also depend upon temperature (see for example reference [18]).

We further extend these considerations to include the effect of impurities. It is found that impurities suppress the FFLO phase for both conventional and unconventional superconductors. However, we also find that impurities lead to qualitatively different (T, H) phase diagrams for conventional (s-wave) and unconventional (non-s-wave) superconductors (see figures 2 and 3). This difference is most easily understood by looking at the coefficients κ and β. For conventional superconductors it is known that β is unchanged by non-magnetic impurities (this is a consequence of Anderson's theorem) while κ is changed. The point on the $[T, H(T)]$ line at which κ changes sign is pushed to lower temperatures with impurities (which illustrates that impurities suppress the FFLO phase). Consequently, the normal-to-FFLO transition in the clean limit is replaced by a first-order normal-to-uniform superconducting transition. For unconventional superconductors, impurities change *both* the κ- and β-coefficients, due to the inapplicability of Anderson's theorem. It is found that the points on the $[T, H(T)]$ line for which $\kappa = 0$ and $\beta = 0$ move to lower temperatures with increasing impurity concentration. The point $\beta = 0$ is more rapidly suppressed than the point $\kappa = 0$. This implies that the initial instability to the FFLO phase is to an FF phase ($\Psi \sim \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}$) as opposed to the LO phase ($\Psi \sim \cos \boldsymbol{q} \cdot \boldsymbol{r}$) that is typically encountered. We are not aware of any other report on the stability of an FF phase. The results here also indicate that the first-order normal-to-uniform superconductor phase transition does not occur for unconventional superconductors.

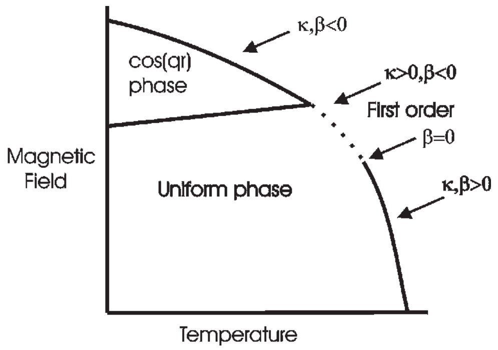

Figure 2. The qualitative phase diagram for conventional superconductors with non-magnetic impurities.

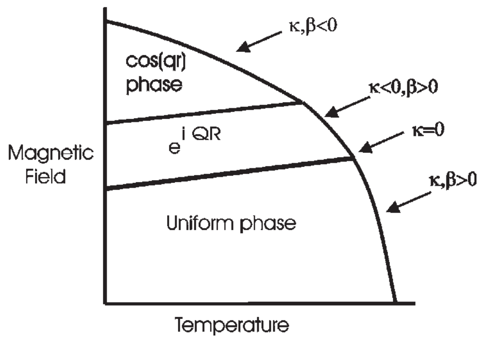

Figure 3. The qualitative phase diagram for unconventional superconductors with non-magnetic impurities.

2. Ginzburg–Landau theory

Consider the Hamiltonian

$$\hat{H} = \int \mathrm{d}\boldsymbol{x} \sum_{\sigma} \Psi_{\sigma}^{\dagger}(\boldsymbol{x})[T(\boldsymbol{x}) + U(\boldsymbol{x}) + 2\sigma\mu B]\Psi_{\sigma}(\boldsymbol{x}) + \hat{V}_{int} \tag{1}$$

where $T(\boldsymbol{x})$ represents the kinetic energy and takes the form $-\nabla^2/(2m) - \epsilon_F$ for a free electron and more generally takes the form $T(\boldsymbol{x}) = \epsilon(\boldsymbol{k} = \mathrm{i}\boldsymbol{\nabla})$ for a band with dispersion $\epsilon(\boldsymbol{k})$ measured from the Fermi energy ϵ_F, $U(\boldsymbol{x})$ is the disorder potential and satisfies $\langle U(\boldsymbol{x})\rangle = 0$ and $\langle U(\boldsymbol{x})U(\boldsymbol{x}')\rangle = n_i W \delta^d(\boldsymbol{x} - \boldsymbol{x}')$, n_i is the concentration of impurities, and $\mu = g\mu_B/2$ is the magnetic moment of the electron. We will primarily be interested in singlet pairing in the ground state; so we neglect interactions between electrons with the same spin. The pairing interaction ($\hat{V}_{int}$) is taken to have the separable form

$$\hat{V}_{int} = -V_0 \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}} f_{\boldsymbol{k}} f_{\boldsymbol{k}'}^{*} c_{\boldsymbol{k}+\boldsymbol{q}/2,\uparrow}^{\dagger} c_{-\boldsymbol{k}+\boldsymbol{q}/2,\downarrow}^{\dagger} c_{-\boldsymbol{k}'+\boldsymbol{q}/2,\downarrow} c_{\boldsymbol{k}+\boldsymbol{q}/2,\uparrow}. \tag{2}$$

$f(\boldsymbol{k})$ describes the gap dependence on the Fermi surface and is defined to satisfy $\sum_{\boldsymbol{k}} |f_{\boldsymbol{k}}|^2 = 1$. It is also understood that a cut-off exists in momentum space such that only electrons that are close enough to the Fermi surface interact with each other. After taking the appropriate Fourier transforms the interaction in real space takes the form

$$\hat{V}_{int} = -V_0 \int \mathrm{d}\boldsymbol{x}\, \mathrm{d}\boldsymbol{x}'\, \mathrm{d}\boldsymbol{R}\, f(\boldsymbol{x}) f^*(\boldsymbol{x}') \Psi_\uparrow^\dagger\left(\boldsymbol{R} + \frac{\boldsymbol{x}}{2}\right) \Psi_\downarrow^\dagger\left(\boldsymbol{R} - \frac{\boldsymbol{x}}{2}\right) \times \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{x}'}{2}\right) \Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{x}'}{2}\right) \tag{3}$$

where

$$f(\boldsymbol{x}) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} f_k \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}$$

and V is the volume of the system (note that this definition of $f(\boldsymbol{x})$ implies $\int \mathrm{d}\boldsymbol{x}\, |f(\boldsymbol{x})|^2 = 1$). One may also describe the system using an Euclidean action in terms of Grassman variables:

$$S[\Psi, \overline{\Psi}] = S_0[\Psi, \overline{\Psi}] - \int_0^\beta \mathrm{d}\tau\, V_0 \int \mathrm{d}\boldsymbol{x}\, \mathrm{d}\boldsymbol{x}'\, \mathrm{d}\boldsymbol{R}\, f(\boldsymbol{x}) f^*(\boldsymbol{x}') \times \overline{\Psi}_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{x}}{2}, \tau\right) \overline{\Psi}_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{x}}{2}, \tau\right) \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{x}'}{2}, \tau\right) \Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{x}'}{2}, \tau\right) \tag{4}$$

where S_0 is the action for free electrons, and τ is the imaginary time. The partition function is

$$Z = \int \mathrm{D}\overline{\Psi}\, \mathrm{D}\Psi\, \mathrm{e}^{-S[\Psi, \overline{\Psi}]}. \tag{5}$$

We now decouple the quartic term in S by introducing a pair of Hubbard–Stratonovich fields $\Delta(\boldsymbol{R}, \tau)$ and $\overline{\Delta}(\boldsymbol{R}, \tau)$, which will become the superconducting order parameter:

$$S[\Psi, \overline{\Psi}, \Delta, \overline{\Delta}] = S_0 - \int_0^\beta \mathrm{d}\tau \int \mathrm{d}\boldsymbol{R}\, \mathrm{d}\boldsymbol{r} \left[\Delta(\boldsymbol{R}, \tau) f(\boldsymbol{r}) \overline{\Psi}_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \tau\right) \overline{\Psi}_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \tau\right) + \overline{\Delta}(\boldsymbol{R}, \tau) f^*(\boldsymbol{r}) \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \tau\right) \Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \tau\right)\right] + \int_0^\beta \mathrm{d}\tau \int \mathrm{d}\boldsymbol{R}\, \frac{|\Delta(\boldsymbol{R}, \tau)|^2}{V_0}. \tag{6}$$

With this decoupling, the fermionic action becomes quadratic, and can be integrated out, after which we obtain an effective action in terms of the order parameter $\Delta(\boldsymbol{R}, \tau)$:

$$S_e[\Delta, \overline{\Delta}] = \int_0^\beta \mathrm{d}\tau\, \mathrm{d}\boldsymbol{R}\, \frac{|\Delta(\boldsymbol{R}, \tau)|^2}{V_0} - \log Z[\Delta, \overline{\Delta}] \tag{7}$$

where

$$Z[\Delta, \overline{\Delta}] = \int \mathrm{D}\overline{\Psi}\, \mathrm{D}\Psi\, \exp\left\{-S_0[\Psi, \overline{\Psi}] + \int_0^\beta \mathrm{d}\tau \int \mathrm{d}\boldsymbol{R}\, \mathrm{d}\boldsymbol{r} \left[\Delta(\boldsymbol{R}, \tau) f(\boldsymbol{r}) \times \overline{\Psi}_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \tau\right) \overline{\Psi}_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \tau\right) + \overline{\Delta}(\boldsymbol{R}, \tau) f^*(\boldsymbol{r}) \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \tau\right) \Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \tau\right)\right]\right\}. \tag{8}$$

The mean-field solution corresponds to the saddle point of $S_e[\Delta, \overline{\Delta}]$:

$$\left.\frac{\delta S_e[\Delta, \overline{\Delta}]}{\delta \overline{\Delta}(\boldsymbol{R})}\right|_{\Delta=\Delta_s} = \frac{\Delta_s(\boldsymbol{R})}{V_0} - \left.\frac{\delta \log Z[\Delta, \overline{\Delta}]}{\delta \overline{\Delta}(\boldsymbol{R})}\right|_{\Delta=\Delta_s} = \frac{\Delta_s(\boldsymbol{R})}{V_0} - \int \mathrm{d}\boldsymbol{r}\, f(\boldsymbol{r}) \left\langle \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}\right) \Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}\right) \right\rangle_{\Delta_s} = 0 \tag{9}$$

where $\langle\ \rangle_{\Delta_s}$ stands for quantum and thermal averaging in the presence of the pairing field $\Delta_s(\boldsymbol{R})$. Here we have assumed a static saddle point, so Δ_s has no τ-dependence.

The functional integral formalism can be used to derive the effective Ginzburg–Landau free energy, in the vicinity of the second-order normal-to-uniform superconductor transition line $[T, H(T)]$. This has been done for the short-range attractive interactions (that give rise to s-wave pairing) [23]. Our starting point is the effective action, equation (7). Near $[T, H(T)]$, we may make two simplifications: (i) we may neglect the τ-dependence of Δ as we expect the thermal fluctuations to dominate the quantum fluctuations; (ii) we may expand S_e in powers of Δ. The quadratic terms take the form

$$S_e^{(2)}[\Delta, \overline{\Delta}] = \beta \int \mathrm{d}\boldsymbol{R}\, \frac{|\Delta(\boldsymbol{R})|^2}{V_0} - \int \mathrm{d}\boldsymbol{R}\, \mathrm{d}\boldsymbol{R}'\, Q(\boldsymbol{R}, \boldsymbol{R}')\overline{\Delta}(\boldsymbol{R})\Delta(\boldsymbol{R}') \tag{10}$$

where

$$\begin{aligned} Q(\boldsymbol{R}, \boldsymbol{R}') &= \left.\frac{\delta^2 \log Z}{\delta\Delta(\boldsymbol{R})\,\delta\overline{\Delta}(\boldsymbol{R}')}\right|_{\Delta=0} \\ &= \int_0^\beta \mathrm{d}\tau_1 \int_0^\beta \mathrm{d}\tau_2 \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\, f(\boldsymbol{r}) f^*(\boldsymbol{r}') \\ &\quad \times \left\langle \Psi_\downarrow\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \tau_2\right)\Psi_\uparrow\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \tau_2\right)\overline{\Psi}_\uparrow\left(\boldsymbol{R}' + \frac{\boldsymbol{r}'}{2}, \tau_1\right)\overline{\Psi}_\downarrow\left(\boldsymbol{R}' - \frac{\boldsymbol{r}'}{2}, \tau_1\right)\right\rangle_c \\ &= \int_0^\beta \mathrm{d}\tau_1 \int_0^\beta \mathrm{d}\tau_2 \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\, f(\boldsymbol{r}) f^*(\boldsymbol{r}') \\ &\quad \times G_{0,\downarrow}\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \boldsymbol{R}' - \frac{\boldsymbol{r}'}{2}; \tau_2 - \tau_1\right) G_{0,\uparrow}\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \boldsymbol{R}' + \frac{\boldsymbol{r}'}{2}; \tau_2 - \tau_1\right) \\ &= \sum_{\mathrm{i}\omega_n} \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\, f(\boldsymbol{r}) f^*(\boldsymbol{r}') \\ &\quad \times G_{0,\downarrow}\left(\boldsymbol{R} - \frac{\boldsymbol{r}}{2}, \boldsymbol{R}' - \frac{\boldsymbol{r}'}{2}; \mathrm{i}\omega_n\right) G_{0,\uparrow}\left(\boldsymbol{R} + \frac{\boldsymbol{r}}{2}, \boldsymbol{R}' + \frac{\boldsymbol{r}'}{2}; -\mathrm{i}\omega_n\right). \end{aligned} \tag{11}$$

The quartic term takes the form

$$S_e^{(4)}[\Delta, \overline{\Delta}] = -\frac{1}{2} \int \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, \mathrm{d}\boldsymbol{R}_3\, \mathrm{d}\boldsymbol{R}_4\, R(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, \boldsymbol{R}_4)\Delta(\boldsymbol{R}_1)\overline{\Delta}(\boldsymbol{R}_2)\Delta(\boldsymbol{R}_3)\overline{\Delta}(\boldsymbol{R}_4) \tag{12}$$

where

$$\begin{aligned} R(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, \boldsymbol{R}_4) &= \int_0^\beta \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, \mathrm{d}\tau_3\, \mathrm{d}\tau_4 \int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, \mathrm{d}\boldsymbol{r}_3\, \mathrm{d}\boldsymbol{r}_4\, f(\boldsymbol{r}_1) f^*(\boldsymbol{r}_2) f(\boldsymbol{r}_3) f^*(\boldsymbol{r}_4) \\ &\quad \times G_{0,\uparrow}\left(\boldsymbol{R}_4 - \frac{\boldsymbol{r}_4}{2}, \boldsymbol{R}_1 - \frac{\boldsymbol{r}_1}{2}; \tau_4 - \tau_1\right) G_{0,\downarrow}\left(\boldsymbol{R}_4 + \frac{\boldsymbol{r}_4}{2}, \boldsymbol{R}_3 + \frac{\boldsymbol{r}_3}{2}; \tau_4 - \tau_3\right) \\ &\quad \times G_{0,\uparrow}\left(\boldsymbol{R}_2 - \frac{\boldsymbol{r}_2}{2}, \boldsymbol{R}_3 - \frac{\boldsymbol{r}_3}{2}; \tau_2 - \tau_3\right) G_{0,\downarrow}\left(\boldsymbol{R}_2 + \frac{\boldsymbol{r}_2}{2}, \boldsymbol{R}_1 + \frac{\boldsymbol{r}_1}{2}; \tau_2 - \tau_1\right). \end{aligned} \tag{13}$$

We will need the sixth-order term as well, whose explicit expression (that involves the product of six Green's functions) is not included here. The above quadratic and quartic terms apply for a particular impurity configuration. We will average over impurity distributions when calculating the form of the free energy. We assume that the gap function that appears above corresponds to the gap function averaged over impurities and that we can ignore impurity-induced correlations in the gap function and between the gap function and the single-particle Green's functions. To proceed further, the impurity-averaged correlation functions $\langle GG\rangle$ and $\langle GGGG\rangle$ must be calculated. We determine these within the Born approximation and much of the derivation follows that of Werthamer for conventional s-wave superconductors [24].

The impurity-averaged normal Green's functions are

$$\overline{G}_{0,\sigma}(\boldsymbol{k};\mathrm{i}\omega_n) = 1\Big/\left(\mathrm{i}\omega_n + \mathrm{i}\frac{1}{2\tau}\,\mathrm{sgn}\,\omega_n - \epsilon_{\boldsymbol{k}} + 2\sigma\mu B\right) \tag{14}$$

where $1/(2\tau) = \Gamma = \pi n_i W N(0)$ and σ is 1/2 (−1/2) for $\uparrow$ ($\downarrow$). Consider the average

$$\begin{aligned}\overline{Q}(\boldsymbol{x}_1, \boldsymbol{y}_1; \boldsymbol{x}_2, \boldsymbol{y}_2; \mathrm{i}\omega_n) &= \langle G_{0,\downarrow}(\boldsymbol{x}_1, \boldsymbol{y}_1; \mathrm{i}\omega_n) G_{0,\uparrow}(\boldsymbol{x}_2, \boldsymbol{y}_2; -\mathrm{i}\omega_n)\rangle_{imp} \\ &= \overline{Q}(\boldsymbol{x}_1 - \boldsymbol{y}_2, \boldsymbol{y}_1 - \boldsymbol{y}_2, \boldsymbol{x}_2 - \boldsymbol{y}_2; \mathrm{i}\omega_n)\end{aligned}$$

due to translational invariance. Summing the usual ladder diagrams shown in [24] gives the self-consistent solution

$$\begin{aligned}\overline{Q}(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3; \mathrm{i}\omega_n) &= \overline{G}_{0,\downarrow}(\boldsymbol{R}_1 - \boldsymbol{R}_2; \mathrm{i}\omega_n)\overline{G}_{0,\uparrow}(\boldsymbol{R}_3; -\mathrm{i}\omega_n) \\ &\quad + n_i W \int \mathrm{d}\boldsymbol{R}\, \overline{G}_{0,\downarrow}(\boldsymbol{R}_1 - \boldsymbol{R}; \mathrm{i}\omega_n)\overline{Q}(0, \boldsymbol{R}_2 - \boldsymbol{R}, \boldsymbol{R}_3 - \boldsymbol{R}; \mathrm{i}\omega_n) \\ &\quad \times \overline{G}_{0,\uparrow}(\boldsymbol{R}; -\mathrm{i}\omega_n).\end{aligned} \tag{15}$$

This can be solved after taking the Fourier transforms with respect to $\boldsymbol{R}_1$, $\boldsymbol{R}_2$, and $\boldsymbol{R}_3$:

$$\begin{aligned}\overline{Q}(\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3; \mathrm{i}\omega_n) &= \overline{G}_{0,\uparrow}(\boldsymbol{k}_1; \mathrm{i}\omega_n)\overline{G}_{0,\downarrow}(\boldsymbol{k}_2; -\mathrm{i}\omega_n) \\ &\quad \times \left[V\delta_{\boldsymbol{k}_1,-\boldsymbol{k}_2} + \frac{n_i W \overline{G}_{0,\uparrow}(\boldsymbol{k}_3; \mathrm{i}\omega_n)\overline{G}_{0,\downarrow}(\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3; -\mathrm{i}\omega_n)}{1 - (n_i W/V)\sum_{\boldsymbol{k}} \overline{G}_{0,\uparrow}(\boldsymbol{k}; \mathrm{i}\omega_n)\overline{G}_{0,\downarrow}(\boldsymbol{k} + \boldsymbol{k}_2 + \boldsymbol{k}_3; -\mathrm{i}\omega_n)}\right].\end{aligned} \tag{16}$$

Substituting this result into equation (11) gives

$$\begin{aligned}Q(\boldsymbol{R}, \boldsymbol{R}') &= \frac{1}{V}\sum_{\boldsymbol{q}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{R}-\boldsymbol{R}')} \sum_{\boldsymbol{k},\boldsymbol{k}',\mathrm{i}\omega_n} f_{\boldsymbol{k}} f^*_{\boldsymbol{k}'} \overline{G}_{0,\uparrow}\left(\boldsymbol{k} + \frac{\boldsymbol{q}}{2}; \mathrm{i}\omega_n\right)\overline{G}_{0,\downarrow}\left(\boldsymbol{k}' - \frac{\boldsymbol{q}}{2}; -\mathrm{i}\omega_n\right) \\ &\quad \times \left[V\delta_{\boldsymbol{k},\boldsymbol{k}'} + \frac{n_i W \overline{G}_{0,\uparrow}(\boldsymbol{k}' + \boldsymbol{q}/2; \mathrm{i}\omega_n)\overline{G}_{0,\downarrow}(\boldsymbol{k} - \boldsymbol{q}/2; -\mathrm{i}\omega_n)}{1 - (n_i W/V)\sum_{\boldsymbol{p}} \overline{G}_{0,\uparrow}(\boldsymbol{p} - \boldsymbol{q}/2; \mathrm{i}\omega_n)\overline{G}_{0,\downarrow}(\boldsymbol{p} + \boldsymbol{q}/2; -\mathrm{i}\omega_n)}\right].\end{aligned} \tag{17}$$

Note that the form of the vertex corrections found here is not the same as for conventional s-wave superconductors. In particular, when deriving the terms up to second order in the gradients, the vertex corrections vanish for unconventional superconductors. However, for higher-order gradient terms, the vertex corrections are not zero.

The impurity-averaged correlation function that appears in δS_4 is less straightforward to calculate. For the terms in the free energy that are fourth order in the order parameter, we consider only up to second order in the gradients of the order parameter. In this case the non-zero diagrams have the same form as those that contribute in the s-wave case [24].

After performing the appropriate Taylor series expansions, the following GL free energy for hexagonal and square lattices is found (this expression is valid only for non-s-wave superconductors ($\langle f_{\boldsymbol{k}}\rangle = 0$)):

$$\begin{aligned}F &= \alpha|\Delta|^2 + \beta|\Delta|^4 + \kappa|\nabla\Delta|^2 + \delta|\nabla^2\Delta|^2 + \mu|\Delta|^2|\nabla\Delta|^2 + \eta[(\Delta^*)^2(\nabla\Delta)^2 + (\Delta)^2(\nabla\Delta^*)^2] \\ &\quad + \nu|\Delta|^6 + \tilde{\delta}|(\nabla_x^2 - \nabla_y^2)\Delta|^2\end{aligned} \tag{18}$$

in which the coefficients are

$$\alpha = -N(0)[\ln(T_c^0/T) + \pi K_1 - \pi K_1(\Gamma = 0, B = 0)] \tag{19}$$

$$\beta = \frac{\pi N(0)}{4}(\langle|f(\boldsymbol{k})|^4\rangle K_3 - \Gamma K_4) \tag{20}$$

$$\kappa = \frac{\pi N(0)\langle \boldsymbol{v}_\perp^2(\boldsymbol{k})|f(\boldsymbol{k})|^2\rangle}{8} K_3 \tag{21}$$

$$\delta = -\frac{\pi N(0)\langle|f(\boldsymbol{k})|^2 \boldsymbol{v}_\perp^4(\boldsymbol{k})\rangle}{64} K_5 \tag{22}$$

$$\mu = 8\eta = -\frac{\pi N(0)\langle \boldsymbol{v}_\perp^2(\boldsymbol{k})|f(\boldsymbol{k})|^4\rangle}{4}\left(K_5 - \frac{\Gamma}{\langle|f(\boldsymbol{k})|^4\rangle}K_6\right) \tag{23}$$

$$\tilde{\delta} = \frac{\pi N(0)\langle|f(\boldsymbol{k})|^2(v_x^2(\boldsymbol{k}) - v_y^2(\boldsymbol{k}))^2\rangle}{64}(K_5 + \Gamma\tilde{K}_6) \tag{24}$$

$$\nu = -\frac{\pi N(0)}{8}\left(\langle|f(\boldsymbol{k})|^6\rangle K_5 - \frac{3\Gamma\langle|f(\boldsymbol{k}|^4\rangle}{2}K_6 + 2\Gamma^2 K_7\right) \tag{25}$$

where

$$K_n = (2T)^{1-n}\frac{1}{\pi^n}\,\mathrm{Re}\left(\sum_{\nu=0}^{\infty}\frac{1}{(\nu+z)^n}\right) \tag{26}$$

and where

$$z = \frac{1}{2} - \mathrm{i}\frac{\mu B}{2\pi T} + \frac{\Gamma}{2\pi T} \qquad \tilde{K}_6 = (2T)^{-5}\frac{1}{\pi^6}\,\mathrm{Re}\left[\sum_{\nu=0}^{\infty}\frac{1}{(\nu+z)^5(\nu+\frac{1}{2}-\mathrm{i}\mu B/\{2\pi T\})}\right].$$

The $\tilde{\delta}$-term does not appear for a hexagonal lattice. For an orthorhombic lattice the following terms also appear in the free energy:

$$\begin{aligned}\delta F = {} & \tilde{\kappa}(|\nabla_x\Delta|^2 - |\nabla_y\Delta|^2) + \tilde{\mu}|\Delta|^2(|\nabla_x\Delta|^2 - |\nabla_y\Delta|^2) \\ & + \tilde{\eta}\left[((\nabla_x\Delta)^2 - (\nabla_y\psi)^2)(\Delta^*)^2 + ((\nabla_x\Delta^*)^2 - (\nabla_y\Delta^*)^2)(\Delta)^2\right] \\ & + \delta_2\left\{[(\nabla_x^2 + \nabla_y^2)\Delta][(\nabla_x^2 - \nabla_y^2)\Delta]^* + [(\nabla_x^2 + \nabla_y^2)\Delta]^*[(\nabla_x^2 - \nabla_y^2)\Delta]\right\}.\end{aligned} \tag{27}$$

The coefficients $\tilde{\kappa}$, $\tilde{\mu}$, and $\tilde{\eta}$ are given respectively by κ, μ, η, with $\boldsymbol{v}_\perp^2$ replaced by $(v_x^2 - v_y^2)$, and the coefficient δ_2 is given by δ with $\boldsymbol{v}_\perp^4$ replaced by $\boldsymbol{v}_\perp^2(v_x^2 - v_y^2)$. The free energy is the main result of this paper.

3. s-wave superconductors

Here we review the known results concerning the FFLO phase for a conventional s-wave superconductor and show how it arises from the free energy. As mentioned in the introduction, the only two coefficients that are required to study the instability from the normal phase into the FFLO phase near the tricritical point are κ and β. For a conventional s-wave superconductor (for which $f_{\boldsymbol{k}}$ is a constant) these can easily be determined by following Werthamer's derivation [24] (note that the above free energy does not apply here since $\langle f_{\boldsymbol{k}}\rangle \neq 0$):

$$\kappa_s = \frac{\pi N(0)\langle \boldsymbol{v}_\perp^2(\boldsymbol{k})\rangle}{8}\tilde{K}_3 \tag{28}$$

$$\beta = \frac{\pi N(0)}{4}K_3(\Gamma = 0) \tag{29}$$

where

$$\tilde{K}_3 = (2T)^{-2}\frac{1}{\pi^3}\,\mathrm{Re}\left[\sum_{\nu=0}^{\infty}\frac{1}{(\nu+\frac{1}{2}-\mathrm{i}\mu B/\{2\pi T\})^2(\nu+\frac{1}{2}-\mathrm{i}\mu B/\{2\pi T\}+\Gamma/\{2\pi T\})}\right]. \quad (30)$$

The coefficient β does not depend upon the impurity concentration; this is in agreement with Anderson's theorem. The second-order normal-to-uniform superconductor phase line $[T, H(T)]$ is given by $\alpha(\Gamma = 0) = 0$ and is shown in figure 4. Note that once $\kappa < 0$ or $\beta < 0$, the phase line $[T, H(T)]$ no longer denotes the true normal-to-superconductor phase line. Numerical evaluation of κ_s and β shows that in the clean limit both κ and β vanish at $T = 0.56T_c$. This point is the tricritical point. The phase diagram is shown in figure 1. When impurities are added, numerical evaluations show that κ vanishes at a lower temperature than that at which β vanishes (note that the presence of impurities does not change β). In this case there is a first-order superconducting transition to a homogeneous phase for $T \leqslant 0.56T_c$. Once $\beta < 0$, then the normal-to-superconductor instability line is no longer given by figure 4. To determine whether there exists an FFLO phase for some arbitrary impurity concentration requires a calculation that goes beyond the GL free energy presented here. This is because the GL theory is only valid close to the transition at $T = 0.56T_c$ (note that the GL theory can be used to study the transition into the FFLO phase if the impurity concentration is small enough). The calculations of Bulaevskii and Guseinov for layered superconductors indicate that there is no FFLO phase at $T = 0$ when $\Gamma/T_c > 0.6$ [25]. The qualitative phase diagram in the presence of impurities is shown in figure 2.

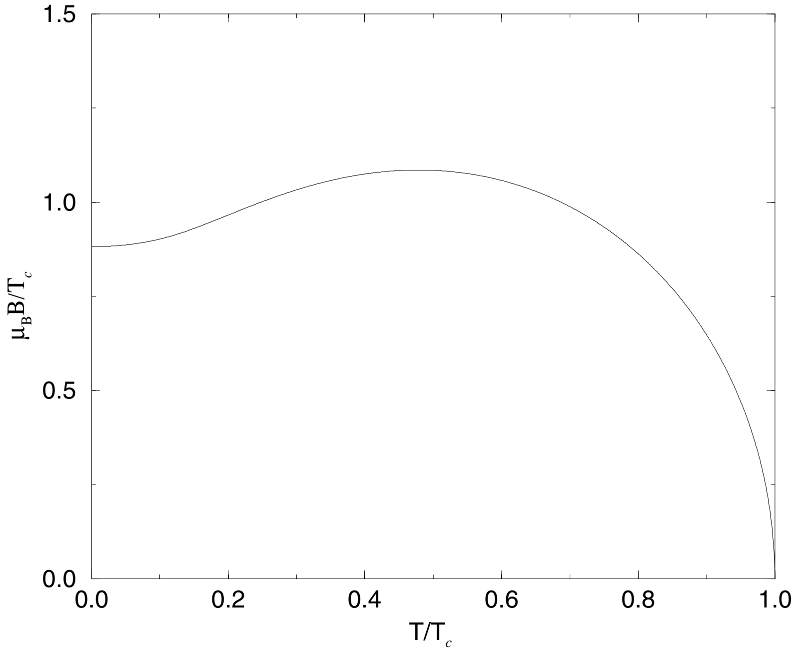

Figure 4. The second-order normal-to-uniform superconducting phase boundary for s-wave superconductors. This line defines $[T, H(T)]$ when there are no impurities present. This is the boundary on which κ and β are determined. Note that for $T \leqslant 0.56T_c$ this phase boundary will *not* coincide with the actual normal-to-superconducting phase boundary (the transition will either be to a non-uniform (FFLO) phase or will be first order).

4. Unconventional superconductors

The last section demonstrated that for T near $0.56T_c$ the GL theory accurately reproduced the phase diagram for conventional superconductors. Here we apply the same approach to unconventional superconductors where it turns out that the GL theory is more powerful. This is the case because the transition from the normal state to the superconducting state is second order for all fields and impurity concentrations for unconventional superconductors. For conventional superconductors this transition is sometimes first order, which limits the applicability of GL theory. For example, the GL theory for unconventional superconductors can give the maximum impurity concentration that allows the FFLO phase to exist; it was not able to do this for s-wave superconductors. As a concrete example we study a d-wave superconductor ($f_{\boldsymbol{k}} \propto k_x^2 - k_y^2$) with a cylindrical Fermi surface. Choosing some other $f_{\boldsymbol{k}}$ will not change the qualitative form of the phase diagrams (provided that $\langle f_{\boldsymbol{k}} \rangle = 0$). The clean-limit phase diagram is qualitatively the same as that for the s-wave case. In fact, the clean-limit theory indicates that the FFLO phase appears for $T < 0.56T_c$ independently of the order parameter symmetry. When impurities are added, the main conclusion is that κ vanishes at a higher temperature than that at which β vanishes when these quantities are evaluated on the phase boundary $[T, H(T)]$ (see figure 5 and figure 6 for the temperature evolutions of κ and β). This implies that there is no first-order transition from the normal state to a uniform superconducting state, but rather a second-order transition into an FFLO phase. The temperature at which $\kappa = 0$ gives the maximum temperature that allows the existence of the FFLO phase (we call this temperature T_F). This is in sharp contrast to what happens in s-wave superconductors, where a first-order phase boundary separates the normal and uniform superconducting state for temperatures just above the point at which β

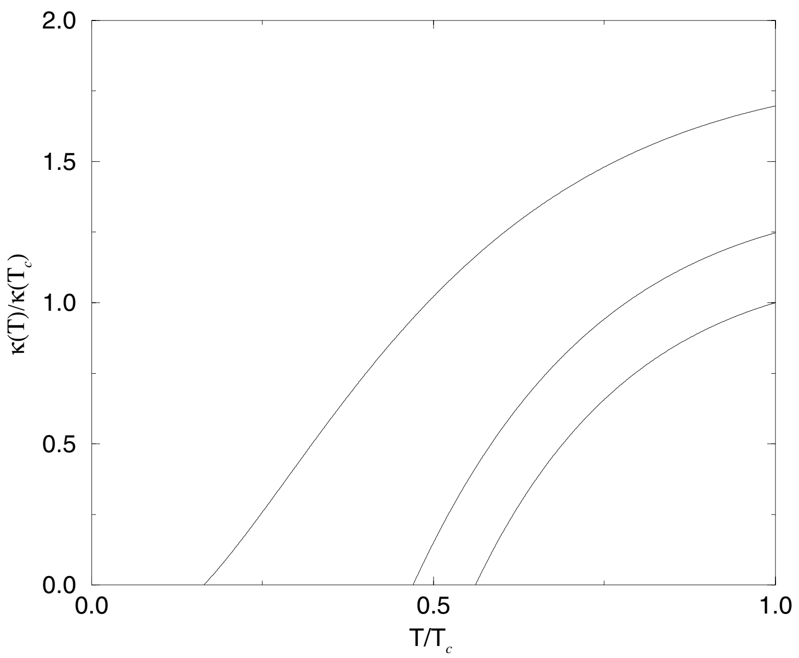

Figure 5. $\kappa(T)/\kappa(T_c)$ on the phase line $[T, H(T)]$ for d-wave superconductors. The curves from top to bottom at $T = T_c$ correspond to $\Gamma/T_c = 0.6$, $\Gamma/T_c = 0.3$, and $\Gamma/T_c = 0.0$ respectively.

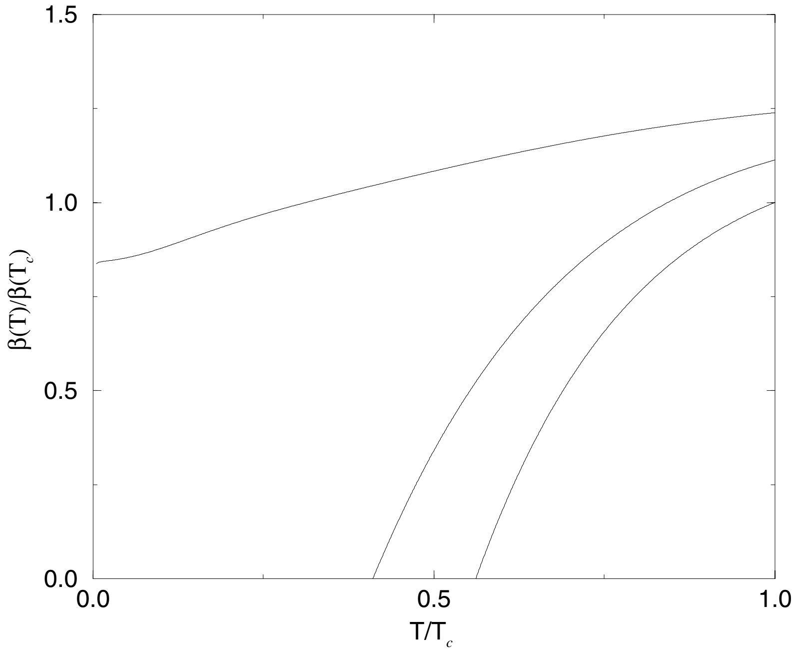

Figure 6. $\beta(T)/\beta(T_c)$ on the phase line $[T, H(T)]$ for d-wave superconductors. The curves from top to bottom at $T = T_c$ correspond to $\Gamma/T_c = 0.6$, $\Gamma/T_c = 0.3$, and $\Gamma/T_c = 0.0$ respectively.

vanishes. Figure 7 shows how T_F varies as the impurity concentration is increased (note that impurities also suppress T_c; hence we plot T_F/T_c as a function of T_c/T_{c0} since the latter is an experimentally measurable quantity). This figure indicates that the FFLO phase survives a considerable impurity concentration; only for $\Gamma/T_c \geqslant 0.6$ does the FFLO phase cease to exist (superconductivity is destroyed when $\Gamma/T_c \geqslant 0.88$).

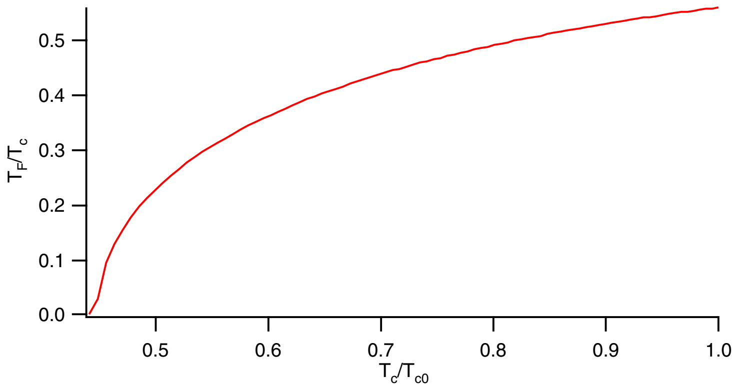

Figure 7. The maximum temperature (T_F) for which the FFLO phase can exist as a function of the transition temperature (which is suppressed by impurities).

The structure of the FFLO phase can also be addressed within the GL theory in the neighbourhood of the tricritical point (given by $\kappa = 0$ on the phase line $[T, H(T)]$). To do this we compare the free energy for three different phases: (1) $\Delta_1 = \Delta_0$ (the uniform phase),

(2) $\Delta_2 = \Delta_0 e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ (the FF phase), and (3) $\Delta_3 = \Delta_0 \cos(\boldsymbol{q}\cdot\boldsymbol{r})$ (the LO phase). We note here that terms $O(\Delta^6)$ do not need to be included in the calculations done here because the terms $O(\Delta^4)$ are positive. Also the minimization with respect to the orientation of $\boldsymbol{q}$ for Δ_2 and Δ_3 implies that $\boldsymbol{q}$ is oriented along the nodes for all impurity concentrations. This agrees with earlier calculations that go beyond the GL theory in the clean limit [15, 18]. After minimizing with respect to $\boldsymbol{q}$ the resulting free energies are

$$F_1 = \alpha|\Delta|^2 + \beta|\Delta|^4 \tag{31}$$

$$F_2 = \left(\alpha - \frac{\kappa^2}{4\delta}\right)|\Delta|^2 + \beta_2|\Delta|^4 \tag{32}$$

$$F_3 = \left(\alpha - \frac{\kappa^2}{4\delta}\right)|\Delta|^2 + \beta_3|\Delta|^4 \tag{33}$$

where

$$\beta_2 = \beta - \frac{3\kappa\eta}{\delta} \qquad \beta_3 = \frac{3}{2}\beta - \frac{5\kappa\eta}{2\delta}$$

(where we have used $\mu = 8\eta$). It is clear that when $\kappa = 0$, $F_1 = F_2 < F_3$ which implies that $\alpha = 0$ and $\kappa = 0$ gives the tricritical point where the normal, uniform superconducting, and FF superconducting phases meet. Note that the FF phase is stable while the LO phase is not at the tricritical point, since $\beta > 0$ (the FF phase is never stable in the s-wave case). For temperatures below that of the tricritical point the phase transition from the normal phase into the FFLO phase is given by $\alpha = \kappa^2/(4\delta)$. Intriguingly, along this phase line, β changes sign. This implies a first-order transition between the FF and the LO phases. This can be seen by comparing F_2 and F_3 which is equivalent to comparing β_2 and β_3. If $\beta = 0$ and $\kappa < 0$ then $0 < \beta_3 < \beta_2$ which implies $F_3 < F_2$, implying that there is a phase transition between the FF and the LO phases. For the singlet superconductors considered here, the FF phase should exhibit a spin current.

A detailed calculation was carried out for an impurity concentration for which $T_c/T_{c0} = 0.573$ (where T_{c0} is the transition temperature with no impurities present). Figure 8 shows the resulting phase diagram calculated within the GL theory. Note that GL theory gives a reasonable description of the phase diagram in this case because it is valid along the entire normal-to-superconducting phase transition boundary. For other impurity concentrations

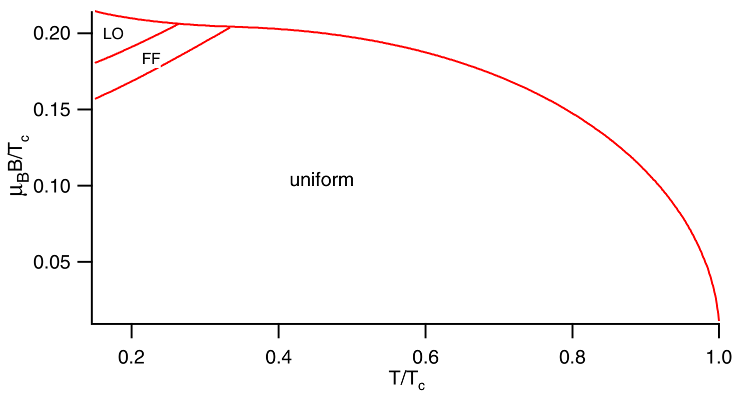

Figure 8. The phase diagram for a d-wave superconductor with T_c suppressed by impurities such that $T_c/T_{c0} = 0.573$. 'FF' refers to an order parameter of the form $\Delta = \Delta_0 e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ while 'LO' refers to an order parameter of the form $\Delta = \Delta_0 \cos(\boldsymbol{q}\cdot\boldsymbol{r})$.

the phase diagram is similar. If multiple scattering from the impurities becomes important (e.g. going beyond the Born approximation to a T-matrix treatment), then it is found that the region of the phase diagram where the FF phase appears shrinks [26].

5. Conclusions

In conclusion, we have derived the GL free energy for singlet superconductors in the presence of a Zeeman field and non-magnetic impurities. This free energy was used to examine the resulting phase diagram. It was shown that the phase diagrams for unconventional superconductors and conventional superconductors are qualitatively different in the presence of impurities. In particular the first-order normal-to-uniform superconductor phase transition that exists for conventional superconductors does not exist for unconventional superconductors. Also, for unconventional superconductors, impurities induce a change in the structure of the FFLO phase. In the clean limit the FFLO phase is described by an order parameter of the form $\cos(\boldsymbol{q}\cdot\boldsymbol{r})$ (LO) while impurities stabilize an $e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ (FF) type of order parameter.

Acknowledgments

This work was supported by NSF DMR-9971541, the Research Corporation, and the A P Sloan Foundation (KY), and by NSF DMR-9527035 and the State of Florida (DFA).

References

[1] Fulde P and Ferrell A 1964 *Phys. Rev.* **135** A550
[2] Larkin A I and Ovchinnikov Y N 1965 *Sov. Phys.–JETP* **20** 762
[3] Aslamazov L G 1969 *Sov. Phys.–JETP* **28** 773
[4] Gloos K *et al* 1993 *Phys. Rev. Lett.* **70** 501
[5] Yin G and Maki K 1993 *Phys. Rev.* B **48** 650
[6] Norman M R 1993 *Phys. Rev. Lett.* **71** 3391
[7] Burkhardt H and Rainer D 1994 *Ann. Phys., Lpz.* **3** 181
[8] Shimahara H 1994 *Phys. Rev.* B **50** 12 760
Shimahara H 1997 *J. Phys. Soc. Japan* **66** 541
Shimahara H 1998 *J. Phys. Soc. Japan* **67** 736
Shimahara H 1998 *J. Phys. Soc. Japan* **67** 1872
[9] Murthy G and Shankar R 1995 *J. Phys.: Condens. Matter* **7** 9155
[10] Dupuis N 1995 *Phys. Rev.* B **51** 9074
[11] Modler R *et al* 1996 *Phys. Rev. Lett.* **76** 1292
[12] Tachiki M *et al* 1996 *Z. Phys.* B **100** 369
[13] Gegenwart P *et al* 1996 *Ann. Phys., Lpz.* **5** 307
[14] Shimahara H, Matsuo S and Nagai K 1996 *Phys. Rev.* B **53** 12 284
[15] Maki K and Won H 1996 *Czech. J. Phys.* **46** 1035
[16] Samohkin K V 1997 *Physica* C **274** 156
[17] Buzdin A I and Kachkachi H 1997 *Phys. Lett.* A **225** 341
[18] Yang K and Sondhi S L 1998 *Phys. Rev.* B **57** 8566
[19] Symington J A *et al* 2001 *Synth. Met.* **170** 711
[20] Pickett W E, Weht R and Shick A B 1999 *Phys. Rev. Lett.* **83** 3713
[21] Yang K and Agterberg D F 2000 *Phys. Rev. Lett.* **84** 4970
[22] Yang K 2001 *Phys. Rev.* B **63** 140511
[23] Popov V N 1987 *Functional Integrals and Collective Excitations* (Cambridge: Cambridge University Press)
[24] Werthamer N R 1969 *Superconductivity* ed R D Parks (New York: Dekker)
[25] Bulaevskii L N and Guseinov A A 1976 *Sov. J. Low Temp. Phys.* **2** 140
[26] Agterberg D F 2001 unpublished