Surface pair-density-wave superconducting and superfluid states

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Fulde, Ferrell and Larkin, Ovchinnikov predicted inhomogeneous superconducting and superfluid ground states, spontaneously breaking translation symmetries (FFLO states). In this paper, we demonstrate that the transition from the FFLO to normal state as a function of temperature or increased Fermi surface splitting is not a direct one. Instead the system has additional phase transition to a different state where pair-density-wave superconductivity (or superfluidity) exists only on the boundaries of the system while the bulk of the system is normal. The surface pair-density-wave state is very robust and can exist for much larger fields and temperatures than FFLO state.

In regular BCS theory, formation of Cooper pairs, binding together two electrons with opposite spin and opposite momentum results in a uniform superconducting state [1, 2]. In 1964, Fulde, Ferrell and Larkin, Ovchinnikov independently predicted that under certain conditions there should appear an inhomogeneous state in the presence of a strong magnetic field, where Zeeman splitting of the Fermi surfaces leads to the formation of Cooper pairs with non-zero total momentum [3, 4]. Similar inhomogeneous states can form and are of great interest in cold-atom gases [5, 6] and in color superconducting states of quarks that are expected to form in cores of neutron stars [7, 6, 8]. Various predictions indicate that the FFLO state may host many rich physical phenomena including topological defects and phase transitions associated with these defects [9–11]. Other interesting studies include the orbital third critical magnetic field [12] as well as states in samples with nontrivial geometries [13, 14] and multiple competing inhomogeneous states in two dimensional systems [15]. For a more detailed review of the FFLO state, see Refs. [16–18].

The anticipated interesting properties made this state a highly sought after yet there is still no universally accepted experimental proof. The orbital effect is significantly stronger than the paramagnetic effect in most superconductors, hindering observations of the FFLO state. More specifically the upper critical orbital field must be significantly larger than the Chandrasekhar-Clogston limit [19, 20] for an FFLO regime to exist. Materials where possible FFLO states were discussed are heavy fermions superconductors [21], layered organic superconductors [22] such as $\lambda$-(BETS)$_2$FeCl$_4$ [23, 24] and $\beta^+$-salt [25] and iron-based superconductors [26]. Among the direct experimental probes to identify this state, it has been suggested to study the Josephson effect [27] and Andreev bound states [28].

In this paper we report that on the phase diagrams of superconductors featuring FFLO state should rather generically appear another state that has a form of surface pair-density-wave superconductivity. We find that as the Zeeman splitting field or temperature is increased, superconductivity disappears only in the bulk of the system but a sample should transition into a state with superconducting surface.

The Ginzburg-Landau description of superconductors in the presence of Zeeman splitting was derived from microscopic theory in Ref. [29]. The free energy functional reads $F[\psi] = \int_\Omega F d^d x$ where the free energy density $F$ is

$$ F = \alpha |\psi|^2 + \beta |\nabla \psi|^2 + \gamma |\psi|^4 + \delta |\nabla^2 \psi|^2 + \mu |\psi|^6 $$

where $\psi$ is a complex field referred to as the superconducting order parameter. The coefficients $\alpha, \gamma$ and $\mu$ depend on the applied Zeeman splitting field $H$ and temperature $T$ accordingly

$$\begin{align*}
\alpha &= -\pi N(0)(K_1(H,T) - K_1(H_0(T),T)) \\
n &\approx N(0) \frac{H - H_0(T)}{2\pi T} \text{Im} \left[ \Psi^{(1)} \left( \frac{1}{2} - i \frac{H_0(T)}{2\pi T} \right) \right], \\
\gamma &\approx \frac{\pi N(0) K_3(H_0(T),T)}{4}, \\
\mu &\approx -\frac{\pi N(0) K_5(H_0(T),T)}{8}
\end{align*}$$

where $N(0)$ is the electron density of states at the Fermi surface and we have defined the functions

$$ K_n(H,T) = \frac{2T}{\zeta(2)} \left( \frac{1}{\zeta(n)} \right)^n \text{Re} \left[ \Psi^{(n-1)}(z) \right] $$

where $z = 1/2 - iH/2\pi T$ and $\Psi^{(n)}$ is the polygamma function of order $n$. The function $H_0(T)$ indicate where $\alpha$ changes sign and is defined implicitly by the equation

$$ \ln \left( \frac{T_\text{c}}{T} \right) = \text{Re} \left[ \Psi^{(0)} \left( \frac{1}{2} - i \frac{H_0(T)}{2\pi T} \right) - \Psi^{(0)} \left( \frac{1}{2} \right) \right] $$

where $T_\text{c}$ is the critical temperature above which the normal state is entered. The remaining coefficients are given as $\beta = \beta v_F^2 \gamma$, $\delta = \delta v_F^4 \nu$ and $\mu = \mu v_F^4 \nu$ where $v_F$ is the Fermi velocity and $\delta, \beta, \mu$ are positive constants that depend on the dimensionality $d$. In one dimension we have $\beta = 1$, $\delta = 1/2$, $\mu = 4$ and in two dimensions we have $\beta = 1/2$, $\delta = 3/16$, $\mu = 2$. In the parameter regime in which $\beta$ is negative, inhomogeneous order parameters may be energetically favourable. For a derivation of the Ginzburg-Landau expansion in cold atoms see Ref. [5].
Typically considered structures of the order parameter are the so-called Fulde-Ferrell (FF) state $\psi_{\text{FF}} = |\psi_{\text{FF}}| e^{iqx}$ and the Larkin-Ovchinnikov (LO) state $\psi_{\text{LO}} = |\psi_{\text{LO}}| \cos qx$. For an infinite system, assuming that the order parameter vanishes close to the tricritical point, the free energy density of these states can be minimized analytically by neglecting higher order terms, resulting in the conclusion that the LO state has energetically preferred over the FF state. The second order phase transition into the normal state occurs at $\alpha = \alpha^c_{\text{bulk}} = \beta^2/4\delta$. In general, the optimal order parameter structure is found by solving the equation of motion associated with the free energy functional (called Ginzburg-Landau equations in this context). This was done analytically in the one dimensional case for an infinite sized superconductor, resulting in elliptic sine solutions [29]. The sinusoidal oscillations are recovered by approaching the transition into the normal state. We solve the equation in a superconductor with boundaries. We consider the case of the real order parameter. The solutions [29]. The sinusoidal oscillations are recovered by approaching the transition into the normal state. We solve the equation in a superconductor with boundaries. We consider the case of the real order parameter. The equation of motion can be derived through variational principles. By mapping $\psi \mapsto \psi + v$ in the free energy functional, where $v$ is some small arbitrary perturbation, we find to linear order in $v$ using Eq. 1

$$F[\psi + v] = F[\psi] + \delta F_{\text{bulk}} + \delta F_{\text{surface}}$$

where

$$\delta F_{\text{bulk}} = 2 \int_\Omega \left( \alpha \psi - \beta \nabla^2 \psi + 2 \gamma \psi^3 + \delta \nabla^4 \psi \right) \psi \, dx$$

$$\delta F_{\text{surface}} = 2 \int_{\partial \Omega} \left( \left[ \beta + \frac{\delta}{4} \right] \nabla \psi - \delta \nabla^3 \psi \right) \, n \cdot dS$$

where $n$ is the normal vector to the boundary $\partial \Omega$. By setting $\delta F_{\text{bulk}} = 0$ we find the equation of motion and by setting $\delta F_{\text{surface}} = 0$ we find the two boundary conditions:

$$\left( \left[ \beta + \frac{\delta}{4} \right] \nabla \psi - \delta \nabla^3 \psi \right) \cdot n = 0, \quad \nabla^2 \psi = 0.$$  

It is convenient to rescale the theory in the regime where $\beta$ is negative by defining the dimensionless quantities $\bar{\psi} = \psi/|\psi|, \, \bar{\alpha} = \alpha/(\alpha U(N(0))), \, \bar{x} = q_0 x / v_F$ where $|\psi| = -\gamma/2\nu, \, \alpha U = \gamma^2/4\nu$ and $\delta^2 = -\beta/2\delta$. The free energy can thus be written $F[\bar{\psi}] = N(0) \bar{\psi}^2/\alpha U|\psi|^2 + q_0^4 \bar{F}[\bar{\psi}]$ where $\bar{F}[\bar{\psi}] = \int_{\bar{\Omega}} \bar{\nabla}^d \bar{\psi}$, in which the rescaled free energy density is identical to Eq. 1 where the coefficients have been replaced accordingly $\alpha \mapsto \bar{\alpha}, \beta \mapsto \bar{\beta}$ and so on where $\bar{\gamma} = -2\delta = -2\beta^2/\delta$ and $\bar{\mu} = \hat{\beta} \mu / \delta$. Consequently there is only one free parameter $\bar{\alpha}$ in the rescaled theory to vary, which parametrizes changes in both temperature and Zeeman splitting field.

Having derived boundary conditions, we will now numerically minimize the free energy for a superconductor with boundaries using the finite element method within FreeFem++ framework [30] and the nonlinear conjugate gradient algorithm, while varying $\bar{\alpha}$. The associated free energy is calculated in order to locate phase transition from the uniform state to the FFLO state and the transition into the normal state. Both one dimensional and two dimensional domains are studied.

We find that the free energy remains negative for $\bar{\alpha}$ larger than the critical value $\bar{\alpha}^c_{\text{bulk}} = 2$ and in two dimensions $\bar{\alpha}^c_{\text{bulk}} = 4/3$. The origin of it is the formation of a distinct surface pair-density-wave (PDW) superconducting state which has a superconducting gap on the boundaries of the system but not in its bulk. The obtained order parameter structure has the form of damped oscillation with an amplitude that vanishes in the bulk but remains non-zero close to the boundaries. The boundary states are observable in both one and two dimensional systems. The results have been verified by altering the system size and found that for sufficiently large system the surface state is independent of system size.

The origin of the appearance of the surface PDW state is the following: besides the inhomogeneous order parameter, the bulk FFLO state has inhomogeneous energy density. The numerical solutions for one and two dimensional cases are plotted in Fig. 1. As the system approaches the phase transition from the bulk FFLO to bulk normal state, the energy gain from the areas with negative energy density are becoming balanced off by the areas with positive energy density. However, if the system has a boundary, a solution can be found where the boundary cuts off a segment of inhomogeneous solutions with positive energy and has a decaying oscillatory configuration of the order parameter extending to a certain length scale in the bulk. That is a decaying solution near boundary starting with a negative energy segment should be stable even when the system does not support FFLO state in the bulk. Indeed the numerical solutions clearly show that the boundaries are characterized by negative energy density as seen in Fig. 1, resulting in stability of surface PDW state for large $\bar{\alpha}$.

The existence of a surface PDW state in an semi-infinite system $\Omega = [0, \infty)$ can be proven analytically. To that end we use an variational ansatz of the form

$$\psi(x) = \Delta \cdot e^{-kx} \cos(qx + \phi)$$

where the parameters $\Delta, k, q$ and $\phi$ should be found such that the free energy is minimized, subject to the boundary conditions. The surface PDW to normal transition occurs when the energy is minimal with $\Delta = 0$. When the transition into the normal state is of second order, it is sufficient to consider terms proportional to $|\Delta|^2$ in...
Due to superconductivity existing only in a thin layer the free energy. In addition the boundary condition in Eq. 10 takes the simpler form \((\beta \nabla \psi - \delta \nabla^3 \psi) \cdot n = 0\) close to the transition into the normal state. Carrying out the minimization analytically, we find that the free energy associated with the surface PDW state remains negative until \(\alpha = \alpha_c^{\text{surface}} = 4\alpha_c^{\text{bulk}}\). Since this is an ansatz-based analytical calculation, it should underestimate the critical temperature. The numerical results indicate that the transition to the surface superconductivity occurs at only about a 20% larger value of \(\alpha\), which implies that the variational ansatz in Eq. 12 captures fairly well the solution for surface PDW state.

We can draw the phase diagram with respect to \(H\) and \(T\) for the one dimensional system, as shown in Fig. 2. The inhomogeneous regime is split into two parts; the bulk FFLO state and the surface PDW state. The regime of surface PDW state extends on the phase diagram significantly larger than the bulk FFLO regime.

In conclusion, we have studied superconducting or superfluid systems supporting Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state. We found that at elevated temperatures or for strong splitting of Fermi surfaces such systems support a state where surface of the sample is a pair-density-wave (PDW) superconductor or superfluid while the bulk of the system is normal. Correspondingly, when the temperature is increased the system has two phase transitions: first superconductivity disappears in the bulk of the system while surfaces remain superconducting. The system goes fully normal only at a higher temperature. In the considered regime we found that the surface PDW state is more robust than FFLO and extends to much larger values of Fermi surface splitting and temperatures. In superconducting materials that should be detectable in calorimetry experiments resulting in the main specific heat feature below superconducting phase transition: associated with the disappearance of the gap in the bulk of the system while the system retains superconductivity due to the surface PDW state. Due to superconductivity existing only in a thin layer in the surface PDW state, another expected experimental signature is a concomitant increase of magnetic field penetration lengths for fields perpendicular to the superconducting layer. If we decrease the size of our system, the areas of surface PDW superconductivity overlap indicating that small superconductors should have PDW superconductivity in their bulk in large range of fields and temperatures, at least at the level of a mean field theory. In cold atoms [5], the surface PDW state can be directly observed for experiments realizing sharp potential walls. Finally the results have implications for the

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models of color superconductivity in the neutron stars cores, which is widely believed to be of FFLO type [7]. The results imply that analogue of the surface color superconducting PDW state may form on the boundary between color superconducting quark matter and dense nuclear matter.

**Note added** When this work was in preparation, there appeared a microscopic study within Bogoliubov-de-Gennes formalism reporting a persistent FFLO state in very small superconductors, giving it a different explanation [31]. Although the studied system sizes there appear to be too small to observe the PDW surface state, the microscopic solutions are consistent with our Ginzburg-Landau-based conclusions here and in [15] that surface effect make modulated superconducting states more robust.

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