

Broken Translational and Time-Reversal Symmetry in Unconventional Superconducting Films

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We demonstrate that films of an unconventional (*d*-wave) superconductor at temperatures $T \lesssim 0.43T_c$ can exhibit unusual superconducting phases. The new ground states beside the broken gauge and the point group symmetries can spontaneously break (i) continuous translational symmetry and form periodic order parameter structures in the plane of the film, or (ii) time-reversal symmetry and develop a supercurrent flowing along the film. These states are the result of the strong transverse inhomogeneity present in films with a thickness of several coherence lengths. We show a natural similarity between the formation of these states and the Fulde-Ferrell-Larkin-Ovchinnikov state.

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Introduction.—The properties of a superconducting (SC) state in confined geometry will have a defining influence on the minimization of superconducting devices. This is especially true of an unconventional superfluid with an order parameter (OP) that breaks more than one of the normal state symmetries [1–3] and which can be suppressed by interfaces, forming new nonuniform ground states [4]. Such states can exhibit new broken symmetries and currently are the subject of broad theoretical and experimental investigation [5]. They can arise in bulk superconductors under the influence of an external field or pressure. For example, a magnetic field breaks the time-reversal symmetry by inducing supercurrents or, as in the case of the Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state [6,7], results in an oscillating OP that breaks continuous spatial translation symmetry. In unconventional superconductors, new ground states have been predicted to appear spontaneously even in the absence of an externally applied magnetic field. One origin of these states is the interaction of a self-induced magnetic field, caused by distortion of the OP, with the OP itself [8–12]. Other current-carrying states arise near surfaces due to subdominant *d + is* pairing that breaks time-reversal symmetry [13,14]. Finally, new states with triplet structure may appear in quantum wires [15]. Ultimately, the origin of these states lies in the appearance of Andreev states bound to interfaces [4,11,16].

In this Letter, we propose the existence of new ground states with nontrivially broken symmetries that require neither the self-induced magnetic field nor complex subdominant pairing. These states are induced by strong distortion of the OP shape. We consider this problem in the context of a singlet *d*-wave superconductor, when distortion of the OP is caused by confinement to a film or wire. We assume that the thickness of the film is adjustable and that by varying it we are able to drive transitions between different ground states. The simplicity of this model makes the problem more transparent yet allows one to draw general conclusions about a connection of inhomogeneity

and spontaneous symmetry breaking in unconventional pairing states, including superfluid ^3He [17].

Free energy in a film.—We consider a film of a *d*-wave superconductor with pair-breaking surfaces, such that the OP in the film is very nonuniform. This is achieved by orienting a gap node along the film (sketch in Fig. 1). We assume a cylindrical Fermi surface and OP solutions uniform along its axis (*z* direction). Below the superconducting bulk temperature T_c , the OP can be continuously suppressed to zero by reducing the thickness D of the film, eventually reaching the normal state below a critical value of $D^*(T)$ [18]. Our goal is to look for states that have

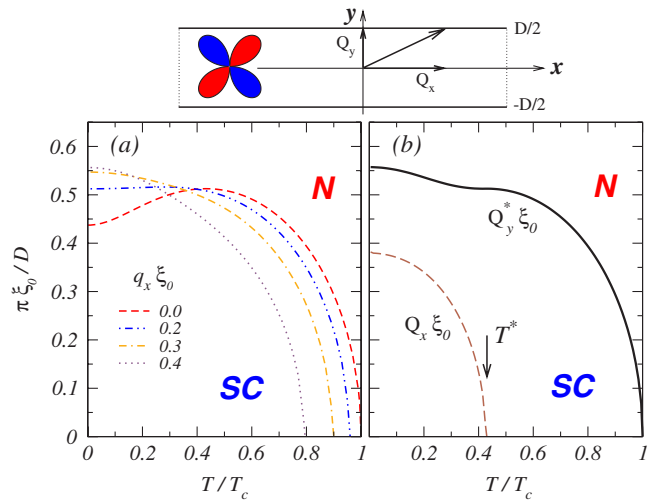


FIG. 1 (color online). A *d*-wave superconductor confined to a film with pair-breaking surfaces. (a) The SC-normal (N) transition as a function of temperature for several q_x -modulated states. At low temperature, transition into a uniform ($q_x = 0$) SC state shows reentrant behavior and is preempted by a transition into a state with finite x modulation; (b) the envelope of various q_x curves gives the maximal confinement vector $Q_y^*(T, Q_x) = \pi/D^*$, plotted together with the corresponding modulation vector $Q_x(T)$. The coherence length $\xi_0 = \hbar v_f / 2\pi T_c$.

more features than just the trivial suppression of the OP near the film's surfaces.

We start with a derivation of the Ginzburg-Landau free energy that describes this transition. For this we solve the microscopic quasiclassical equations [19,20] for the diagonal g and off-diagonal (anomalous) components f and f' of the quasiclassical Green's function $\hat{g}(\mathbf{R}, \hat{\mathbf{p}}; \varepsilon_m)$. The complete set of equations also includes the normalization condition and symmetry relations

$$\begin{aligned} [\varepsilon_m + \frac{1}{2}\mathbf{v}(\hat{\mathbf{p}}) \cdot \nabla_{\mathbf{R}}]f &= ig\Delta(\mathbf{R}, \hat{\mathbf{p}}), & g^2 - ff' &= -\pi^2, \\ f'(\mathbf{R}, \hat{\mathbf{p}}; \varepsilon_m) &= f(\mathbf{R}, \hat{\mathbf{p}}; -\varepsilon_m)^*. \end{aligned} \quad (1)$$

Here $\mathbf{v}(\hat{\mathbf{p}}) = v_f \hat{\mathbf{p}}$ is the Fermi velocity at point $\hat{\mathbf{p}}$ on the

Fermi surface, and $\varepsilon_m = \pi T(2m + 1)$ —Matsubara energy. We assume a separable OP and expand the spatial part in plane waves: $\Delta(\mathbf{R}, \hat{\mathbf{p}}) = \mathcal{Y}(\hat{\mathbf{p}})\sum_{\mathbf{q}}\Delta_{\mathbf{q}}e^{i\mathbf{q}\mathbf{R}}$. The normalized basis function is $\mathcal{Y}(\hat{\mathbf{p}}) = \sqrt{2}\sin 2\phi_{\hat{\mathbf{p}}}$, and the plane wave amplitudes satisfy the self-consistency equation

$$\Delta_{\mathbf{q}} \ln \frac{T}{T_c} = T \sum_{\varepsilon_m} \left\langle \mathcal{Y}(\hat{\mathbf{p}}) \left(f_{\mathbf{q}}(\hat{\mathbf{p}}; \varepsilon_m) - \frac{\pi \Delta_{\mathbf{q}} \mathcal{Y}(\hat{\mathbf{p}})}{|\varepsilon_m|} \right) \right\rangle, \quad (2)$$

that follows from minimization of the free energy functional $\delta\Delta F/\delta\Delta_{\mathbf{q}}^* = 0$, and brackets denote angle average $\langle \dots \rangle = \int \frac{d\phi_{\hat{\mathbf{p}}}}{2\pi} \dots$. Solving Eqs. (1) for f up to third order in $\Delta_{\mathbf{q}}$, we use self-consistency (2) to find the free energy

$$\Delta F = \sum_{\mathbf{q}} I(T, \mathbf{q}) |\Delta_{\mathbf{q}}|^2 + \frac{1}{2} \sum_{\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}_3 + \mathbf{q}_4} K(T, \mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) \Delta_{\mathbf{q}_1}^* \Delta_{\mathbf{q}_2}^* \Delta_{\mathbf{q}_3} \Delta_{\mathbf{q}_4}, \quad (3a)$$

$$I(T, \mathbf{q}) = \ln \frac{T}{T_c} - 2\pi T \sum_{\varepsilon_m > 0} \text{Re} \left\langle \mathcal{Y}^2(\hat{\mathbf{p}}) \left(\frac{1}{\varepsilon_m + i\eta_{\mathbf{q}}} - \frac{1}{\varepsilon_m} \right) \right\rangle, \quad \text{where } \eta_{\mathbf{q}} = \frac{1}{2} \mathbf{v} \cdot \mathbf{q}, \quad (3b)$$

$$K(T, \mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = 2\pi T \sum_{\varepsilon_m > 0} \frac{1}{2} \text{Re} \left\langle \mathcal{Y}^4(\hat{\mathbf{p}}) \frac{\varepsilon_m + i(\eta_{\mathbf{q}_1} + \eta_{\mathbf{q}_2} + \eta_{\mathbf{q}_3} + \eta_{\mathbf{q}_4})/4}{(\varepsilon_m + i\eta_{\mathbf{q}_1})(\varepsilon_m + i\eta_{\mathbf{q}_2})(\varepsilon_m + i\eta_{\mathbf{q}_3})(\varepsilon_m + i\eta_{\mathbf{q}_4})} \right\rangle. \quad (3c)$$

This functional describes a second-order transition from the uniform normal state into a general, modulated superconducting state. For analytic analysis and to make use of the fewest number of plane waves in the OP, we consider perfectly specular film surfaces with boundary condition $f(x, \pm D/2, \hat{\mathbf{p}}; \varepsilon_m) = f(x, \pm D/2, \hat{\mathbf{p}}; \varepsilon_m)$, connecting the incoming $\hat{\mathbf{p}}$ and mirror-reflected $\hat{\mathbf{p}} = \hat{\mathbf{p}} - 2\hat{\mathbf{y}}(\hat{\mathbf{y}} \cdot \hat{\mathbf{p}})$ trajectories at surfaces $y = \pm D/2$. From the self-consistency it follows that the OP at the surfaces is zero due to d -wave symmetry. This ensures the OP form $\Delta(\mathbf{R}) = \sum_{q_x} \Delta_{q_x} e^{iq_x x} \cos \pi y/D$ and thus fixes the y -wave number $q_y = Q_y \equiv \pi/D$. Note that fixed Q_y in $\eta_{\mathbf{q}} = (v_x q_x + v_y Q_y)/2$ [Eqs. (3)] plays the same role as the external magnetic field in $\eta_{\mathbf{q}B} = \mathbf{v} \cdot \mathbf{q}/2 + \mu B$ that enters similar equations describing instability into the FFLO phase in Pauli-limited superconductors [21].

Phase diagram of superconducting state in a film.—We first find the boundary of the superconducting phase and thus look for the largest $Q_y^*(T)$ [narrowest strip $D^*(T)$], where superconductivity first appears. This instability is given by condition $I(T, q_x, Q_y^*) = 0$, and its solution $Q_y^*(T, q_x)$ is shown in Fig. 1(a) for various q_x states. The $q_x = 0$ state, uniform along the film, at low temperature is preempted by states with finite modulation q_x . For any given T we determine the optimal q_x [denoted by $Q_x(T)$] that gives the largest Q_y^* [see Fig. 1(b)] and find that x -modulated states are possible below $T^* \sim 0.43T_c$.

Next, we determine the relative stability of various non-uniform states near this transition. For each instability mode $\mathbf{Q}(T) \equiv (Q_x, Q_y)$, there are three other degenerate modes obtained from this one by reflection of x and/or y coordinates. We consider two principal states obtained by

different combinations of these modes: (i) with two opposite q_x components, corresponding to the amplitude oscillations of the OP, which includes all four degenerate states $\mathbf{q}_{1,2,3,4} = \{(Q_x, Q_y), (Q_x, -Q_y), (-Q_x, -Q_y), (-Q_x, Q_y)\}$, and (ii) with one q_x component, that gives a modulation of the OP phase along the film and therefore a superflow $\mathbf{q}_{1,2} = \{(Q_x, Q_y), (Q_x, -Q_y)\}$.

Near the second-order transition,

$$\Delta F[Q_x, -Q_x] = - \frac{2I^2(T, \mathbf{Q})}{K_1 + 2K_{12} + 2K_{13} + 2K_{14} + 2K_{1234}} \quad \text{for } \Delta(\mathbf{R}) = \Delta_1(e^{iQ_x x} + e^{-iQ_x x}) \cos Q_y y, \quad (4a)$$

$$\Delta F[Q_x] = - \frac{2I^2(T, \mathbf{Q})}{2(K_1 + 2K_{12})} \quad \text{for } \Delta(\mathbf{R}) = \Delta_2 e^{iQ_x x} \cos Q_y y. \quad (4b)$$

Here we use notation $K_1 = K(\mathbf{q}_1, \mathbf{q}_1, \mathbf{q}_1, \mathbf{q}_1)$, $K_{1234} = K(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$, and, for pairs of wave vectors, $K_{ij} = K(\mathbf{q}_i, \mathbf{q}_j, \mathbf{q}_i, \mathbf{q}_j)$. At low temperatures we calculate these coefficients analytically and find that the K_{13} term, corresponding to the two opposite wave vectors $\pm \mathbf{Q}$ ($\mathbf{Q} \nparallel$ node), diverges as $1/T$. This makes the current-carrying state with spontaneously broken time-reversal symmetry the lowest in energy [22]. Numerical evaluation of all K 's shows that the state with a current has the lowest energy at all $T < T^*$. We also find that a transition from a normal to superconducting state is always second order in the film, to be contrasted with bulk Pauli-limited superconductors, where the Δ^4 -term coefficient becomes negative and transition becomes first order at low temperatures [23,24]. In a film, even for $q_x = 0$, we have a wave vector pair $\pm Q_y \neq 0$ and

$K_{12} > 0$, which guarantees a positive sign of $K_1 + 2K_{12}$ in Eq. (4b), even though $K_1 < 0$ at low temperatures.

To fully describe the phase diagram and elucidate the structure of the new phases, we determine the transition between the new phases and the $q_x = 0$ “uniform” condensate deep inside the SC state. We start with the state that breaks translational symmetry and forms periodic modulations of $|\Delta(\mathbf{R})|$ in the film’s plane. In this case, the general form of the OP is similar to one in the FFLO problem [25,26]. Near the normal state instability, $\Delta(x, y) \sim \cos Q_x x \cos Q_y y$ but becomes less harmonic and more domainlike structured along x , as we increase film thickness (Q_y decreases). The distance between neighboring domains grows, and at some critical Q_y^{crit} the last domain wall, that separates two degenerate states at $x = \pm\infty$ with opposite OP profiles $\pm\Delta(y)$, disappears (square-symbol line in Fig. 3). Note, that this transition occurs below unphysical $q_x = 0$ line (thin dots in Fig. 3), as compared with the FFLO problem [25,26]: there is no first-order transition above the $q_x = 0$ line in this case—thus the inhomogeneous phase must cover the entire thermodynamically unstable region. Energetically, the state with the modulated amplitude of the OP gains energy compared with the energy of uniform state from the reduction of pair breaking at the domain walls and the redistribution of the Andreev bound states [17].

Next, we consider a state with phase modulation (superflow), $\Delta(\mathbf{R}) = \Delta \cos Q_y y e^{iQ_x x}$, that carries supercurrent $J_{s,x}(y) = 2N_f T \sum_{\varepsilon_m} \langle v_x(\hat{\mathbf{p}}) g(y, \hat{\mathbf{p}}; \varepsilon_m) \rangle$. We write down a more general form of the OP, $\Delta(x, y) = \Delta_{q_x}(y) \exp(iq_x x)$, and self-consistently determine its amplitude profile and the associated free energy density [27]:

$$\Omega^D(q_x) = \int_{-D/2}^{D/2} \frac{dy}{D} \Delta F^D(q_x, y), \quad (5)$$

as a function of q_x and the film thickness D . Key features of this calculation are shown in Fig. 2. In the main panel, we plot Ω^D as a function of inverse film thickness for several q_x . States with finite superflow are stabilized in films thinner than $D^*(T) = \pi/Q_y^*(T)$. Moreover, their stability region extends beyond that of the $q_x = 0$ state. Since finite q_x induces supercurrent, it can be the ground state only when the total current in the film disappears: $J_{s,x}^D \equiv \rho_s^D(q_x) q_x = \partial \Omega^D(q_x) / \partial q_x = 0$ [16]. The upper critical width D^* is determined by vanishing average superfluid density $\rho_s^{D^*}(0) = 0$. These conditions are possible to satisfy due to backflowing anomalous surface currents carried by Andreev bound states (inset in Fig. 2) [11,14,28].

The complete phase diagram is presented in Fig. 3. Below $T^* \sim 0.43T_c$, two new ground states are possible in superconducting films. The state with spontaneous current and broken time-reversal symmetry takes a large part of the phase space. Under the considered conditions, the state with a modulated amplitude of the OP lies inside the stability region of the current-carrying state and is not realized. However, the relative energies of the two states

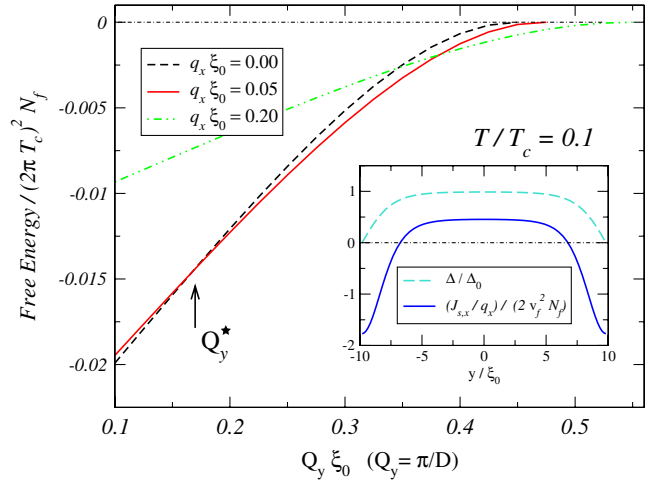


FIG. 2 (color online). Free energy density of a d -wave superconductor confined to a film, as a function of the inverse thickness for $T/T_c = 0.1$. In films with $D < D^* = \pi/Q_y^*$, the states with superflow have lower energy than the $q_x = 0$ state. The inset shows self-consistently calculated order parameter profile $\Delta(y)$ and the current density $J_{s,x}(y)$ for small q_x and $D \lesssim D^*$. The current has anomalous (paramagnetic) contributions near the edges due to Andreev bound states, and Q_y^* marks the point where the average superfluid density in the film $\rho_s \equiv \lim_{q_x \rightarrow 0} J_{s,x}^D / q_x$ vanishes.

may be affected, e.g., by surface roughness. Also note that within numerical precision the lower instability line $D^*(T)$ is nearly straight and extrapolates to the origin.

The qualitative picture for the appearance of the longitudinal modulations of the OP in the film is illustrated by analogy with the FFLO state in Fig. 4. In the FFLO state, modulations of the OP arise to minimize pair breaking caused by pairing of electrons across Zeeman-split Fermi

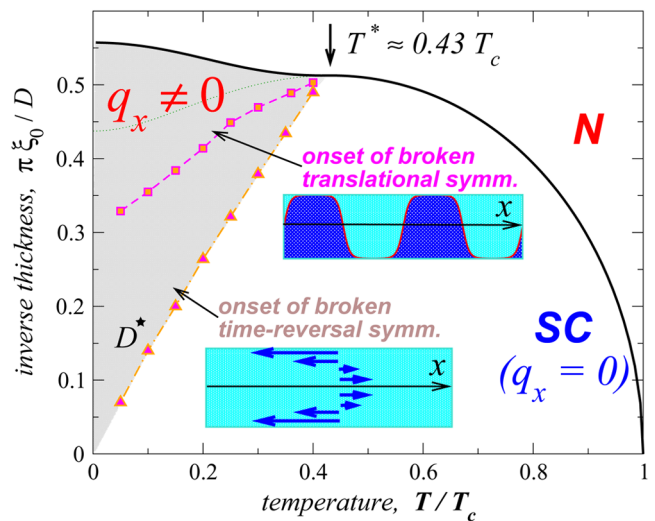


FIG. 3 (color online). The phase diagram of a d -wave superconductor in a film. The shaded region marks the ground state with flowing current. Suppression of this state would open access to the state with broken translational symmetry.

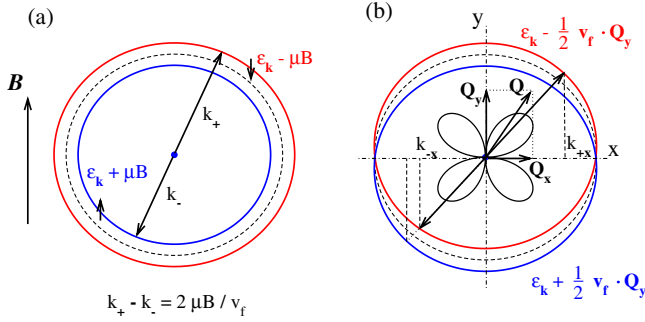


FIG. 4 (color online). (a) Inhomogeneous state of FFLO type, when the pair-forming states with opposite spins belong to different Fermi surfaces, split by a magnetic field; (b) state with spontaneous current along x . The Fermi surface is shifted by fixed center-of-mass flow $\pm Q_y$. Paired states can have additional x momentum Q_x to minimize pair breaking.

surfaces $\varepsilon_{\mathbf{k}} \pm \mu B$ [Fig. 4(a)]. In the strongly inhomogeneous state in the film, the role of magnetic field is played by the fixed confining wave vector Q_y that produces superflow across the film and shifts the Fermi surface vertically, $\varepsilon_{\mathbf{k}} \pm v_y Q_y/2$ [Fig. 4(b)]. Pairs are formed with additional shift Q_x (so that $\mathbf{Q} \nparallel$ node) to minimize pair breaking by the superflow; cf. Ref. [29].

Finally, we remark on the observability of these states. In superconductors, diamagnetic coupling to a (self-induced) magnetic field will modify the phase diagram (Fig. 3). Previous studies of a semi-infinite ($1/D \rightarrow 0$) system [10–12] show that spontaneous surface current appears already at finite temperature, and this indicates that the phase space for $q_x \neq 0$ state may be enlarged. Also, modulated states in confined geometry are less sensitive to the disorder and would persist much longer in dirty samples compared with surface states [10]. In fact, we find that complete suppression of $T^* \rightarrow 0$ by impurities happens only when the corresponding suppression of T_c is 60% (mean free path $\ell \sim 5\xi_0$). It is also reasonable to expect that, as long as the OP has significant gradient across the film, the new superconducting phases are only slightly affected by surface roughness.

Conclusions.—We have studied behavior of a d -wave superconductor in a film geometry. We find that large gradients of the order parameter across the film can be—quite counterintuitively—“relieved” by producing additional modulation along the film. This means that in confined geometry this pairing system may undergo a transition into a state with broken translational or even time-reversal symmetry. Similar behavior occurs in a completely different pairing state (triplet, p -wave) in ^3He films [17], and we suggest that these states are common to unconventional pairing systems, although their exact nature may depend on the structure of the OP. The new ground states are more robust in film or wire geometry than in bulk or semi-infinite systems and should be ob-

servable in superconductors and neutral superfluid ^3He in confinement.

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