Ginzburg-Landau equations for mixed $s+d$ symmetry superconductors

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We derive microscopically the Ginzburg-Landau equations for weak-coupling superconductors with coexisting s and d symmetries. The equations are derived from Gor'kov equations by using the finite temperature Green's-function method. We explore the physical consequences of such Ginzburg-Landau equations.

Superconducting states with mixed s and d symmetry have been proposed for a long time. It is believed that s-d mixing is relevant to the heavy-fermion systems.[1] Most recently, it is suggested some of the anomalous superconducting properties of the high-T_c superconductors could be explained by s-d mixing.[2,3] The description of coexisting s and d symmetry itself is also theoretically interesting. All previous work on mixed s-d state are based on forms of a Ginzburg-Landau (GL) free-energy functional obtained from group-theory arguments. Since many parameters in these theories are not known, it is not clear where the physically relevant regions of the order parameters lie. In our earlier work,[4] we have given the first derivation of the Ginzburg-Landau equations in a purely d-wave superconductor. Here we will derive the Ginzburg-Landau equations for a mixed s- and d-wave superconductor in the weak-coupling limit by using the same method. We will show most parameters in the resulting Ginzburg-Landau equations are fixed by symmetries of the order paramters and thus not "free."

To this end, we begin with the Gor'kov's equations[5]

$$\left\{ i\omega_n - \frac{1}{2m}(-i\nabla + e\mathbf{A})^2 + \mu \right\} \tilde{G}(\mathbf{x},\mathbf{x}',\omega_n) + \int d\mathbf{x}''\ \Delta(\mathbf{x},\mathbf{x}'')F^+(\mathbf{x}'',\mathbf{x}',\omega_n) = \delta(\mathbf{x}-\mathbf{x}'), \quad (1)$$

$$\left\{ -i\omega_n - \frac{1}{2m}(i\nabla + e\mathbf{A})^2 + \mu \right\} F^+(\mathbf{x},\mathbf{x}',\omega_n) + \int d\mathbf{x}''\ \Delta^*(\mathbf{x},\mathbf{x}'')\tilde{G}(\mathbf{x}'',\mathbf{x}',\omega_n) = 0, \quad (2)$$

and derive equations for the $\mathbf{k}$ dependence of the order parameter. Here $\tilde{G}$ and F are, respectively, the single particle and pair propagators. $\omega_n = (2n+1)\pi T$. The self-consistent equation to determine the pair potential is expressed in real space as

$$\Delta^*(\mathbf{x},\mathbf{x}') = V(\mathbf{x}-\mathbf{x}')T\sum_{\omega_n} F^\dagger(\mathbf{x},\mathbf{x}',\omega_n), \quad (3)$$

with $-V(\mathbf{x}-\mathbf{x}')$ as the effective pairing interaction between two charge carriers. When the superconductor is in the vicinity of the onset of superconductivity, $\Delta(\mathbf{x},\mathbf{x}')$ is a small quantity that can be expressed upon. From Eqs. (1) and (2), and iterating Eq. (3) to the third order in Δ for $F^\dagger$ and second order in G, we find

$$\Delta^*(\mathbf{x},\mathbf{y}) = V(\mathbf{x}-\mathbf{y})T\sum_{\omega_n} \left\{ \int d\mathbf{x}'\ d\mathbf{x}''\ \tilde{G}_0(\mathbf{x}',\mathbf{x},-\omega_n)\Delta^*(\mathbf{x}',\mathbf{x}'') \times \left[\tilde{G}_0(\mathbf{x}'',\mathbf{y},\omega_n) - \int d\mathbf{x}_1\ d\mathbf{x}_2\ \tilde{G}_0(\mathbf{x}'',\mathbf{x}_1,\omega_n)\Delta(\mathbf{x}_1,\mathbf{x}_2) \int d\mathbf{x}_3\ d\mathbf{x}_4\ \tilde{G}_0(\mathbf{x}_3,\mathbf{x}_2,-\omega_n)\Delta^*(\mathbf{x}_3,\mathbf{x}_4)\tilde{G}_0(\mathbf{x}_4,\mathbf{y},\omega_n) \right] \right\}, \quad (4)$$

where $\tilde{G}_0$ is the Green's function of free electrons in magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$. In the case that we are interested in where $1/k_F$ (k_F is the Fermi wave number) is much less than the London penetration depth, $\mathbf{A}$ can be treated as a constant over distances of many wavelengths, thus $\tilde{G}_0$ can be related to the zero-field Green's function G_0 via the approximate expression[6,7]

$$\tilde{G}_0(\mathbf{x},\mathbf{x}',\omega_n) \approx G_0(\mathbf{x}-\mathbf{x}',\omega_n)e^{-ie\mathbf{A}(\mathbf{x})\cdot(\mathbf{x}-\mathbf{x}')}, \quad (5)$$

and

$$G_0(\mathbf{x},\omega_n) = \frac{1}{(2\pi)^2}\int d\mathbf{k}\ e^{i\mathbf{k}\cdot\mathbf{x}} \frac{1}{i\omega_n - \xi_\mathbf{k}}, \quad (6)$$

where $\xi_\mathbf{k} = \mathbf{k}^2/2m - \mu$ is the kinetic energy of the charge carrier with mass m measured from the chemical potential μ. And for simplicity, we have assumed the Fermi surface is two dimensional. A third dimension can be easily added to the final equations if needed.

By introducing the center-of-mass coordinates

$$\mathbf{R}=\frac{1}{2}(\mathbf{x}+\mathbf{y}),\quad \mathbf{R}'=\frac{1}{2}(\mathbf{x}'+\mathbf{x}''), \tag{7}$$

and the Fourier transform $\mathbf{k}$, $\mathbf{k}'$ of the relative coordinates

$$\mathbf{r}=\mathbf{x}-\mathbf{y},\quad \mathbf{r}'=\mathbf{x}'-\mathbf{x}'', \tag{8}$$

we obtain, using a Taylor expansion

$$\Delta^*(\mathbf{x}',\mathbf{x}'')\approx e^{\int_x^{x'}\nabla_{\hat{x}}\cdot d\hat{l}+\int_y^{x''}}\nabla_{\hat{y}}\cdot d\hat{l}\,\Delta^*(\mathbf{x},\mathbf{y}) \tag{9}$$

to relate Δ's when their coordinates are close enough,

$$\Delta^*(\mathbf{R},\mathbf{k})=\Delta^*_{(1)}(\mathbf{R},\mathbf{k})+\Delta^*_{(2)}(\mathbf{R},\mathbf{k}), \tag{10}$$

and

$$\begin{aligned}\Delta^*_{(1)}(\mathbf{R},\mathbf{k})=&\int d\mathbf{r}\,e^{-i\mathbf{k}\cdot\mathbf{r}}V(\mathbf{r})\int dR'\,dr'\,\frac{1}{\beta}\sum_{\omega_n}\int\frac{dp\,dq}{(2\pi)^4}e^{ip[R'-R+(r'/2)-(r/2)]+iq[R'-R-(r'/2)+(r/2)]}\frac{1}{-i\omega_n-\xi_p}\frac{1}{i\omega_n-\xi_q}\\&\times e^{i(\mathbf{R}'-\mathbf{R})\cdot\Pi_R+i(\mathbf{r}'-\mathbf{r})\cdot\mathbf{k}'}\int\frac{dk'}{(2\pi)^2}e^{i\mathbf{k}'\cdot\mathbf{r}}\Delta^*(\mathbf{R},\mathbf{k}')\\=&\int\frac{d\mathbf{k}'}{(2\pi)^2}V(\mathbf{k}'-\mathbf{k})\Bigg\{T\sum_{\omega_n}\frac{1}{\omega_n^2+\xi_{\mathbf{k}'^2}}+\frac{T}{2}\sum_{\omega_n}\Bigg[\frac{1}{(2m)^2}\frac{2\xi_{\mathbf{k}'}^2-6\omega_n^2}{(\omega_n^2+\xi_{\mathbf{k}'}^2)^3}(k_x'^2\Pi_x^2+k_y'^2\Pi_y^2)\\&-\frac{1}{2m}\frac{\xi_{\mathbf{k}'}}{(\omega_n^2+\xi_{\mathbf{k}'}^2)^2}\Pi^2\Bigg]\Bigg\}\Delta^*(\mathbf{R},\mathbf{k}'),\quad \Pi=-i\nabla-2eA,\end{aligned} \tag{11}$$

$$\Delta^*_{(2)}(\mathbf{R},\mathbf{k})=-\int\frac{d\mathbf{k}'}{(2\pi)^2}V(\mathbf{k}-\mathbf{k}')T\sum_{\omega_n}\frac{1}{(\omega_n^2+\xi_{\mathbf{k}'}^2)^2}\times|\Delta^*(\mathbf{R},\mathbf{k}')|^2\Delta^*(\mathbf{R},\mathbf{k}'). \tag{12}$$

We expanded the exponential containing the center-of-mass coordinates but that containing the relative coordinates have to be retained.

To obtain the Ginzburg-Landau equations for a mixed s- and d-wave superconductor, we make the following ansatz:[8]

$$V(\mathbf{k}-\mathbf{k}')=V_s+V_d(\hat{k}_x^2-\hat{k}_y^2)(\hat{k}_x'^2-\hat{k}_y'^2), \tag{13}$$

$$\Delta^*(\mathbf{R},\mathbf{k})=\Delta_s^*(\mathbf{R})+\Delta_d^*(\mathbf{R})(\hat{k}_x^2-\hat{k}_y^2), \tag{14}$$

where $\hat{\mathbf{k}}$ is the unit vector in the direction of $\mathbf{k}$. V_d and V_s are both positive, which corresponds to attractive interactions in both s and d pairing channel.

From Eqs. (11), (12) and comparing both sides of Eq. (10) for $\hat{k}$-independent terms and terms proportional to $(\hat{k}_x^2-\hat{k}_y^2)$, we obtain

$$\begin{aligned}\Delta_s^*=&N(0)V_s\Delta_s^*\ln\frac{2e^\gamma\omega_D}{\pi T}-\frac{7\zeta(3)}{8(\pi T)^2}N(0)V_s\Bigg\{\frac{1}{4}v_F^2\Pi^2\Delta_s^*\\&+\frac{1}{8}v_F^2(\Pi_x^2-\Pi_y^2)\Delta_d^*+|\Delta_s|^2\Delta_s^*+|\Delta_d|^2\Delta_s^*\\&+\frac{1}{2}\Delta_d^{*2}\Delta_s\Bigg\},\end{aligned} \tag{15}$$

$$\begin{aligned}\Delta_d^*=&\frac{1}{2}N(0)V_d\Delta_d^*\ln\frac{2e^\gamma\omega_D}{\pi T}-\frac{7\zeta(3)}{8(\pi T)^2}N(0)V_d\Bigg\{\frac{1}{8}v_F^2\Pi^2\Delta_d^*\\&+\frac{1}{8}v_F^2(\Pi_x^2-\Pi_y^2)\Delta_s^*+|\Delta_s|^2\Delta_d^*+\frac{1}{2}\Delta_s^{*2}\Delta_d\\&+\frac{3}{8}|\Delta_d|^2\Delta_d^*\Bigg\}.\end{aligned} \tag{16}$$

Here γ is the Euler constant, $N(0)$ is the density of states at the Fermi surface, v_F is the Fermi velocity, and ω_D is the cutoff frequency for the interactions.

The free energy obtained from the above equations is

$$\begin{aligned}f=&-2\ \ln(Ts/T)|\Delta_s|^2-\ln(T_d/T)|\Delta_d|^2+\alpha\lambda_d\Bigg[|\Delta_s|^4\\&+\frac{3}{8}|\Delta_d|^4+2|\Delta_s|^2|\Delta_d|^2+\frac{1}{2}(\Delta_s^{*2}\Delta_d^2+\Delta_d^{*2}\Delta_s^2)\Bigg]\\&+\frac{1}{4}\alpha\lambda_d v_F^2[2|\Pi\Delta_s^*|^2+|\Pi\Delta_d^*|^2+(\Pi_x^*\Delta_s\Pi_x\Delta_d^*\\&-\Pi_y^*\Delta_s\Pi_y\Delta_d^*+\text{ H.c.})],\end{aligned} \tag{17}$$

where $\alpha=[7\zeta(3)/8][1/(\pi T)^2]$, and $\lambda_d=(1/2)N(0)V_d$. Here we define T_s and T_d to be the apparent superconducting transition temperature for s wave and d wave,

$$N(0)V_s\ln\frac{2e^\gamma\omega_D}{\pi T_s}=1, \tag{18}$$

$$N(0)V_d\ln\frac{2e^\gamma\omega_D}{\pi T_d}=1/2, \tag{19}$$

respectively.

The corresponding expression for the supercurrent can be obtained from Gor'kov's equations:

$$\mathbf{j}(\mathbf{R})=\frac{e\alpha N(0)E_F}{2m}\left[\Delta_s^*\mathbf{\Pi}^*\Delta_s+\frac{1}{2}\Delta_d^*\mathbf{\Pi}^*\Delta_d+\frac{1}{2}(\Delta_s^*\Pi_x^*\Delta_d+\Delta_d^*\Pi_x^*\Delta_s)\hat{\mathbf{x}}-\frac{1}{2}(\Delta_s^*\Pi_y^*\Delta_d+\Delta_d^*\Pi_y^*\Delta_s)\hat{\mathbf{y}}\right]+\text{H.c.} \tag{20}$$

It is interesting to note that in the free energy, the coefficients of the terms $|\Delta_s|^2|\Delta_d|^2$ and $(\Delta_s^{*2}\Delta_d^2+\Delta_d^{*2}\Delta_s^2)$ are both positive and their relative magnitudes guarantee the overall stability of the free energy. Their signs are not known from group-theory arguments but are very crucial for deciding the symmetry of the ground state. Generally, we expect that when T is lower than both transition temperatures, i.e., $T<T_s$ and $T<T_d$, the s-wave and d-wave solution will coexist in the bulk. And because of the positive coefficients of $\Delta_s^{*2}\Delta_d^2$ term, $s+id$ symmetry is favored. When T is between the two transition temperatures, only one symmetry is present in the bulk, depending on which has the higher transition temperature. To see exactly what happens, we have to minimize the free energy in the bulk. We obtain

$$\frac{\partial f}{\partial\Delta_s^*}=-2\ \ln(T_s/T)\Delta_s+\alpha(2|\Delta_s|^2\Delta_s+2|\Delta_d|^2\Delta_s+\Delta_d^2\Delta_s^*)=0, \tag{21}$$

$$\frac{\partial f}{\partial\Delta_d^*}=-\ln(T_d/T)\Delta_d+\alpha\left(\frac{3}{4}|\Delta_d|^2\Delta_d+2|\Delta_s|^2\Delta_d+\Delta_s^2\Delta_d^*\right)=0, \tag{22}$$

and their Hermitian conjugates.

Equations (21) and (22) have different solutions depending on the temperature T. Two obvious solutions are

$$\Delta_s=0,\quad |\Delta_d|^2=\frac{4}{3\alpha}\ln(T_d/T), \tag{23}$$

$$F_d=-\frac{2}{3\alpha}\ln^2T_d/T, \tag{24}$$

and

$$\Delta_d=0,\quad |\Delta_s|^2=\frac{1}{\alpha}\ln(T_s/T), \tag{25}$$

$$F_s=-\frac{1}{\alpha}\ln^2T_s/T. \tag{26}$$

These are the only possible solutions corresponding to $T>T_s$ and $T>T_d$, respectively.

When $T<T_s$ and $T<T_d$, s and d can coexist in two kinds of combinations, $s+d$ or $s\pm id$. For the $s\pm id$ state, we obtain

$$|\Delta_d|^2=\frac{4}{\alpha}\ln\frac{T_d}{T_s}, \tag{27}$$

$$|\Delta_s|^2=\frac{1}{\alpha}\ln\frac{T_s^3}{T_d^2T}, \tag{28}$$

$$F_{s\pm id}=-\frac{1}{\alpha}(3\ \ln^2T_s/T-4\ \ln T_s/T\ \ln T_d/T+2\ \ln^2T_d/T), \tag{29}$$

which requires $T<T_s^3/T_d^2$ and $T_d>T_s$. It can be shown that the $s+d$ state is never stable for our GL free energy.

Thus we have a peculiar situation; when $T_d>T_s$, there will be a second-order transition from d symmetry to $s\pm id$ symmetry at $T^*=T_s^3/T_d^2$. On the other hand, if $T_s>T_d$, there will be no transition from s symmetry to $s+id$ symmetry. This is because of the generic form of coupling between s-wave and d-wave components, which seems to be independent of particular form of interaction, as long as tetragonal symmetry and isotropic Fermi surface are assumed. A plausible explanation of this s and d asymmetry is that the transition from d to $s\pm id$ is one from a state with zero gap nodes to a gapless state, which is expected to lower the free energy; while the transition from s to $s+id$ is not necessarily favored in energy.

The $s+id$ and $s-id$ states are degenerate in energy, and each of them breaks time-reversal symmetry since time reversal transforms Δ to Δ^*. There have been many proposed experimental consequences of the $s+id$ phase, due to the time-reversal breaking property of such a state. There are also calculations done on systems with a second phase transition to mixed s and d symmetry that suggest measurable effects will be observed in the behavior of H_{c2}. Even though such calculations are done in the limit, the coefficients of the mixed terms are treated as a small perturbation, while our microscopic calculation suggests they are actually comparable to the other terms, we believe qualitatively their conclusion remains correct. A detailed calculation of the H_{c2} needs to be done numerically.

Our result also suggests that in tetragonal systems with mixed s and d symmetry, the $s+d$ state is never a stable solution. The $s+d$ state is not only higher in energy than $s\pm id$ states, but it is also not a local minimum of free energy. This surprising conclusion is due to the fact that even though there are many different competing terms in the free energy, their relative sign and magnitude are decided only by two interactions. Since the validity of Ginzburg-Landau ex-

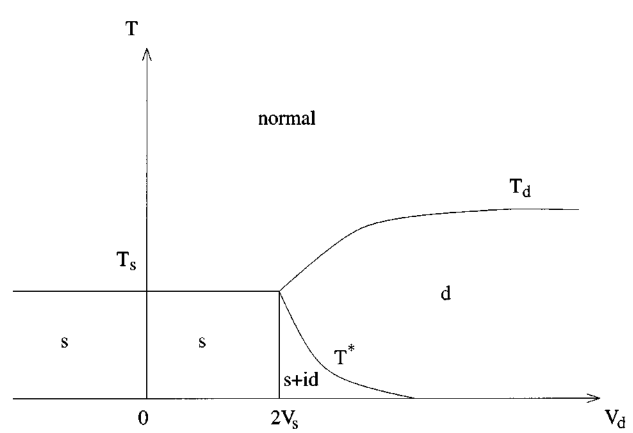

FIG. 1. Phase diagram of coexisting s and d symmetry.

pansion depends on the smallness of the order parameters, our equations are only exact in the limit where T_s and T_d are sufficiently close. It is interesting to note many realistic applications are just in this limit.[2] On the other hand, the condition for the two order parameters to be small, $T-T_s \ll T_s$ and $T-T_d \ll T_d$ are not difficult to meet even for quite different T_d and T_s, and we expect our equations to be qualitatively correct. Our equations can also be extended to the cases $V_s \ll V_d$ or $V_d \ll V_s$. In this limit, it is also close to being exact, since one of the order parameters is automatically small. However, a Padé approximation has to be used in the derivation to avoid unphysical results, just as we did in our previous work.[4] The resulting phase diagram is given in Fig. 1.

In summary, we have derived microscopically the Ginzburg-Landau equations for a weak-coupling superconductor with mixed s and $d_{x^2-y^2}$ symmetry. The phase diagram of such a superconductor is determined. We found that an additional second-order transition will take place within a certain interaction range, i.e., if the apparent transition temperature $T_d > T_s$, but not vice versa. The second transition is to a mixed $s \pm d$ phase which breaks time-reversal symmetry. The Ginzburg-Landau equations that we obtained should provide a convenient starting point for studying various properties of the superconducting state in such a superconductor if they are proved to exist, as many theories have proposed in the past.

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