Boundary conditions on the Ginzburg-Landau equations for anisotropic superconductors

E. A. Shapoval

All-Union Scientific-Research Center for Studies of Surface and Vacuum Properties
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The method of semiclassical trajectories is generalized to the anisotropic case and used to find effective boundary conditions on the Ginzburg-Landau equations at an interface of an anisotropic superconductor with vacuum. Diffusive, specular, and the most general electron reflection laws at the surface are considered. In each case the boundary conditions turn out to be conditions of the third kind with a coefficient the same sign, which indicates a weakening of the order in a surface layer. The absolute value of this coefficient depends on the orientation of the crystallographic axes. In order of magnitude, it is equal to the anisotropy parameter of the energy gap divided by the size of a Cooper pair.

Soon after Bardeen, Cooper, and Schrieffer's derivation of a microscopic theory of superconductivity,[1] Gor'kov showed[3] that the phenomenological equations which had been proposed previously by Ginzburg and Landau[2] for a superconductor near the transition temperature follow from the microscopic theory. Gor'kov also determined the microscopic meaning of the parameters of the Ginzburg-Landau theory. Boundary conditions on the Ginzburg-Landau equations were found from the microscopic theory by De Gennes[4] and Zaitsev.[5] An anisotropic version of the phenomenological equations was proposed by Ginzburg.[6] Their microscopic derivation was continued by Gor'kov and Melik-Barkhudarov.[7] The boundary conditions on these equations, however, have not yet been examined. As we will see below, these boundary conditions turn out to be nontrivial.

1. INITIAL EQUATIONS

In order to find the boundary conditions on the Ginzburg-Landau equations, we must first derive an equation for the order parameter at $T = T_c$. The most convenient way to this is to work from Gor'kov's system of equations. The corresponding equation for an anisotropic superconductor can then be written in the following form in the momentum representation[7]:

$$\Delta^*(\mathbf{p}_1, \mathbf{p}_2) = gT \sum_{\omega} \iiint \frac{d\mathbf{p}_1'\, d\mathbf{p}_2'\, d\mathbf{q}_1\, d\mathbf{q}_2}{(2\pi)^9} \times \delta(\mathbf{q}_1+\mathbf{q}_2-\mathbf{p}_1-\mathbf{p}_2)\, V(\mathbf{q}_1, \mathbf{q}_2; \mathbf{p}_1, \mathbf{p}_2) \times G_{-\omega}(\mathbf{p}_1', \mathbf{q}_1)\, G_{\omega}(\mathbf{p}_2', \mathbf{q}_2)\, \Delta^*(\mathbf{p}_1', \mathbf{p}_2'). \tag{1.1}$$

Here $\Delta^*(\mathbf{p}_1, \mathbf{p}_2)$ is the superconducting order parameter in the momentum representation, $V(\mathbf{q}_1, \mathbf{q}_2; \mathbf{p}_1, \mathbf{p}_2)$ is a dimensionless matrix element of the electron interaction energy, the functions $G_\omega(\mathbf{p},\mathbf{q})$ are the temperature Green's functions of the electrons in the normal state, $\omega = \pi T(2n+1)$, and the summation over integer values of n is cut off at $|\omega|$ on the order of the Debye energy.

In homogeneous problems we would have $\Delta^*(\mathbf{p}_1, \mathbf{p}_2) = \Delta^*(\mathbf{p}_1)\delta(\mathbf{p}_1 + \mathbf{p}_2)$, so that the sum of the momenta is a measure of the inhomogeneity. In inhomogeneous problems, the order parameter changes significantly only over distances on the order of the correlation radius $\xi_0 \sim v/T_c$; these distances are much larger than the interatomic distances. We take Fourier transforms of the sum of the momenta which characterizes the inhomogeneity. The remaining integrals over differences between momenta converge rapidly as we move away from the Fermi surface. In those integrals, we use the change of variables $d(\mathbf{p}_1 - \mathbf{p}_2) = d\mathbf{p} = d\xi d\sigma/v$ ($d\sigma$ is an element of the Fermi surface, v is the corresponding Fermi velocity, and ξ is the energy reckoned from the Fermi level), and we integrate over $d\xi$. As a result we find the following equation for the order parameter:

$$\Delta^*(\mathbf{r}; \mathbf{p}) = \int d\mathbf{r}' \int \frac{d\sigma'}{(2\pi)^3 v'} \int \frac{d\sigma''}{(2\pi)^3 v''} \Delta^*(\mathbf{r}'; \mathbf{p}')\, U(\mathbf{p}'', \mathbf{p})\, gT \times \sum_{\omega} \Phi_{\omega}(\mathbf{r}', \mathbf{p}'; \mathbf{r}, \mathbf{p}''). \tag{1.2}$$

Here the vectors $\mathbf{p}$ determined the corresponding point on the Fermi surface:

$$\Phi_{\omega}(\mathbf{r}', \mathbf{p}'; \mathbf{r}, \mathbf{p}) = \iint d\xi\, d\xi' \iint d\mathbf{r}_1\, d\mathbf{r}_2 G_{\omega}\left(\mathbf{r}' + \frac{\mathbf{r}_1}{2}, \mathbf{r} + \frac{\mathbf{r}_2}{2}\right) \times G_{-\omega}\left(\mathbf{r}' - \frac{\mathbf{r}_1}{2}, \mathbf{r} - \frac{\mathbf{r}_2}{2}\right) \exp(-i\mathbf{p}'\mathbf{r}_1 + i\mathbf{p}\mathbf{r}_2),$$

$$U(\mathbf{p}'', \mathbf{p}) = V(\mathbf{p}'', -\mathbf{p}''; \mathbf{p}, -\mathbf{p}). \tag{1.3}$$

In the particular case of a homogeneous superconductor, in the absence of a field, we would have

$$\Phi_{\omega}(\mathbf{r}', \mathbf{p}'; \mathbf{r}, \mathbf{p}) = (2\pi)^4 (\tilde{m}v)^2 \delta(\sigma'-\sigma)\, \delta(\sigma-\sigma_{\parallel}) \times \exp(-2|\omega||\mathbf{r}-\mathbf{r}'|/v)/(\mathbf{r}-\mathbf{r}')^2. \tag{1.4}$$

Here σ and σ' are the points on the Fermi surface corresponding to the vectors $\mathbf{p}$ and $\mathbf{p}'$; $\sigma_{\parallel}$ is that point on the Fermi surface where the Fermi velocity vector is parallel to the vector $\omega(\mathbf{r} - \mathbf{r}')$; and $(\tilde{m}v)^{-2}$ is the Gaussian curvature of the Fermi surface at this point, which relates the element of solid angle in velocity space to the corresponding element on the Fermi surface, i.e., $do = (\tilde{m}v)^{-2} d\sigma$.

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2. BOUNDARY CONDITIONS FOR DIFFUSE REFLECTION

We consider a semi-infinite anisotropic superconductor filling the half-space $z>0$ and bounded by vacuum. We assume that electrons are reflected diffusely from the interface. Since the motion of the electrons near the Fermi surface is semiclassical, we use the method of semiclassical trajectories proposed in Ref. 8, generalizing it to the present case, that of an anisotropic superconductor. As can be seen from (1.4), the function $\Phi_\omega(\mathbf{r}', \mathbf{p}'; \mathbf{r}, \mathbf{p})$ is related by a $2|\omega|$ Laplace transform to the probability that an electron on the Fermi surface which leaves the point $\mathbf{r}$ with a momentum $\mathbf{p}$ and moves at the Fermi velocity $\mathbf{v}$ will, after a given time, reach the point $\mathbf{r}'$ with a momentum $\mathbf{p}'$. In the absence of a boundary, we must take into account in the calculation of Φ_ω, along with the trajectory which directly connects the point $\mathbf{r}$ and $\mathbf{r}'$, those trajectories which contain a reflection from the boundary of the superconductor. The diffuse reflection law means that an electron colliding with a boundary completely "forgets" its previous momentum and velocity. The probability for reflection with a given momentum and a given velocity is proportional to $v_z\,d\sigma/v$—when there is a complete "memory loss," this is the only possible reflection law which conserves the direction distribution of the electrons after their reflection from the surface.

Assuming that all quantities depend only on the coordinate z, we find

$$\Phi_\omega(z', \mathbf{p}'; z, \mathbf{p}) = \pi\left[\frac{(2\pi)^3 v\delta(\sigma'-\sigma)}{|v_z|}\exp\left(-2\frac{|\omega|\,|z-z'|}{|v_z|}\right) + \frac{1}{\nu\langle|v_z|\rangle}\exp\left(-2\frac{|\omega|z}{|v_z|}-2\frac{|\omega|z'}{|v_z'|}\right)\right]. \tag{2.1}$$

For brevity we are using

$$\langle(\ldots)\rangle = \int\frac{d\sigma}{(2\pi)^3 v\nu}(\ldots), \tag{2.2}$$

where ν is the electron state density at the Fermi level.

The first term in brackets on the right side of (2.1) corresponds to trajectories which connect the points z and z' directly; the second term corresponds to trajectories which contain a diffuse reflection from the boundary. The integral in the denominator in the second term, which is to be carried out over the Fermi half-surface with $v_z>0$, is extended to the entire surface by virtue of the symmetry of the Fermi surface with respect to inversion.

We expand the electron scattering function $U(\mathbf{p}, \mathbf{p}')$ in eigenfunctions of the integral equation

$$\varphi(\mathbf{p}) = \lambda\langle U(\mathbf{p}, \mathbf{p}')\varphi(\mathbf{p}')\rangle', \tag{2.3}$$

where the prime on the average means that the integration is to be carried out over $d\sigma'(\mathbf{p}')$. In the weak-coupling approximation, as Pokrovskiĭ has shown,[9] it is sufficient to retain only the leading term of this expansion, which corresponds to the minimum eigenvalue λ_0. Because of the latitude which remains in the choice of the numerical value of the constant of the electron interaction, we normalize the corresponding eigenfunction by $\langle\varphi_0^2(\mathbf{p})\rangle = 1$. The ordering parameter is then $\Delta^*(z, \mathbf{p}) = \Psi(z)\varphi_0(\mathbf{p})$, and the equation for $\Psi(z)$ becomes

$$\frac{\lambda_0}{\nu g}\Psi(z) = \int_0^\infty dz'\,\Psi(z')\pi T\sum_\omega\tilde{\Phi}_\omega(z, z'), \tag{2.4}$$

$$\tilde{\Phi}_\omega(z, z') = \left\langle\frac{\varphi_0^2(\mathbf{p})}{|v_z|}\exp\left(-2\frac{|\omega|\,|z-z'|}{|v_z|}\right)\right\rangle + \left\langle\varphi_0(\mathbf{p})\exp\left(-2\frac{|\omega|z}{|v_z|}\right)\right\rangle \times\left\langle\varphi_0(\mathbf{p})\exp\left(-2\frac{|\omega|z'}{|v_z|}\right)\right\rangle\langle|v_z|\rangle^{-1}. \tag{2.5}$$

In the absence of an anisotropy of the energy gap we would have $\varphi_0(\mathbf{p}) = 1$, and Eq. (2.4) would have the exact solution $\Psi(z) = \text{const}$, from which we find the standard boundary condition $\mathbf{n}\nabla\Psi = 0$. In the general case with $z \gg \xi_0$ we can ignore the second term in (2.5) and find the asymptotic form of the solution of Eq. (2.4) at $T = T_c$ far from the boundary, $\Psi_0(z) = 1 + \alpha z$. The coefficient α, which determines the effective boundary condition, is calculated in the Appendix. If the anisotropy is slight, as it usually is in a real superconductor, we would have

$$\alpha = \frac{\pi^3 T_c}{7\zeta(3)}\frac{1}{\langle v_z^2\rangle}\left[\langle\varphi_0^2(\mathbf{p})\,|v_z|\rangle - \frac{\langle\varphi_0(\mathbf{p})\,|v_z|\rangle^2}{\langle|v_z|\rangle}\right]. \tag{2.6}$$

From the Cauchy inequality we have $\alpha>0$; i.e., a diffuse surface slightly weakens the order in the surface layer of an anisotropic superconductor. This effect is similar in a sense to that of nonmagnetic impurities.[10]

Taking the gradiant invariance into account, we can write the boundary condition on the Ginzburg-Landau equation in the following form for an anisotropic superconductor in a magnetic field:

$$\mathbf{n}\left(\nabla - 2i\frac{e}{c}\mathbf{A}\right)\Psi = -\alpha\Psi. \tag{2.7}$$

The coefficient α can be expressed in terms of the parameters of the Ginzburg-Landau theory

$$\eta = 7\zeta(3)\varepsilon_F/12(\pi T_c)^2, \quad m_{ij}^{-1} = 3\langle\varphi_0^2(\mathbf{p})v_iv_j\rangle/2\varepsilon_F,$$

as follows:

$$\alpha = \frac{\pi}{8}\frac{1}{T_c\eta m_{zz}^{-1}}\left[\langle\varphi_0^2(\mathbf{p})\,|v_z|\rangle - \frac{\langle\varphi_0|v_z|\rangle^2}{\langle|v_z|\rangle}\right]. \tag{2.8}$$

3. BOUNDARY CONDITIONS FOR SPECULAR REFLECTION

The result derived in the preceding section suggests that we examine the opposite limiting case, that of specular reflection of electrons from the surface, for which the projection of the momentum onto the $z=0$ plane is conserved. The corresponding kernel of the integral equation could be found from the definition of its ω components in terms of the Green's functions in the normal state, (1.3). However, it is simpler to again use the method of semiclassical trajectories; the ultimate result does not depend on the approach taken.

The ω components of the kernel of integral equation (2.4) found in this manner differ from the ω components of (2.5) because of the second term, which now describes specular reflection:

$$\tilde{\Phi}_\omega^{(2)}(z,z')=\left\langle \frac{\varphi_0(\mathbf{p})\varphi_0(\mathbf{p}')}{|v_z'|}\exp\left(-2\frac{|\omega|z}{|v_z|}-2\frac{|\omega|z'}{|v_z'|}\right)\right\rangle. \tag{3.1}$$

Here the Fermi momenta $\mathbf{p}$ and $\mathbf{p}'$ are related by the condition that their projections onto the reflection surface are equal; the z projections of the corresponding Fermi velocities, $\mathbf{v}$ and $\mathbf{v}'$, are oppositely directed. Expression (3.1) is symmetric with respect to z and z' by virtue of the relation $|v_z|d\sigma/v=|v_z'|d\sigma'/v'$. By analogy with the preceding section, we can find the coefficient which determines the boundary condition (2.7):

$$\alpha=\frac{\pi^2T_c}{7\zeta(3)}\frac{1}{\langle v_z^2\rangle}[\langle\varphi_0^2(\mathbf{p})|v_z|\rangle-\langle\varphi_0(\mathbf{p})\varphi_0(\mathbf{p}')|v_z|\rangle]$$
$$=\frac{\pi}{2T_c\eta m_{zz}^{-1}}\langle[\varphi_0(\mathbf{p})-\varphi_0(\mathbf{p}')]^2|v_z|\rangle. \tag{3.2}$$

It follows from this expression that we have $\alpha\geqslant 1$, as in the case of diffuse reflection.

4. ARBITRARY REFLECTION LAW

In the most general case, the reflection law can be described by the phenomenological correlation function $R(\mathbf{p},\mathbf{p}')$, which determines the probability that an electron with momentum $\mathbf{p}$ will go into a state with momentum $\mathbf{p}'$ as a result of reflection. To make the function $R(\mathbf{p},\mathbf{p}')$ symmetric with respect to its arguments, we incorporate in it the probability for the incidence of an electron with a momentum $\mathbf{p}$ on the surface, which is proportional to the projection of its Fermi velocity $|v_z|$. To avoid complicating the equations below with the condition that the integration be carried out over half of the Fermi surface, because the incident electrons are moving in one direction, while the reflected electrons are moving in the other direction, we make use of the symmetry with respect to inversion and set $R(-\mathbf{p},\mathbf{p}')=R(\mathbf{p},-\mathbf{p}')=R(\mathbf{p},\mathbf{p}')$. The condition for conservation of the electron distribution after reflection requires

$$\langle R(\mathbf{p},\mathbf{p}')\rangle=|v_z'|\langle|v_z|\rangle^{-1};\quad \langle R(\mathbf{p},\mathbf{p}')\rangle'=|v_z|\langle|v_z|\rangle^{-1}. \tag{4.1}$$

For diffuse reflection we would have

$$R(\mathbf{p},\mathbf{p}')=|v_zv_z'|\langle|v_z|\rangle^2,$$

while for specular reflection R contains a δ-function which conserves the projection of the momentum onto the reflecting surface.

By the method of semiclassical trajectories we find the second term, corrected for reflection, of the ω component (2.5) of the kernel of integral equation (2.4):

$$\tilde{\Phi}_\omega^{(2)}(z,z')=\left\langle\!\!\left\langle \frac{\varphi_0(\mathbf{p})\varphi_0(\mathbf{p}')}{|v_zv_z'|}\exp\left(-\frac{2|\omega|z}{|v_z|}-\frac{2|\omega|z'}{|v_z'|}\right)\right.\right.$$
$$\left.\left.\times R(\mathbf{p},\mathbf{p}')\right\rangle\!\!\right\rangle'\langle v_z\rangle. \tag{4.2}$$

Using the method outlined in the Appendix, we then find the coefficient which determines the boundary conditions (2.7):

$$\alpha=\frac{\pi^2T_c}{7\zeta(3)}\frac{1}{\langle v_z^2\rangle}\langle(\varphi_0^2(\mathbf{p})|v_z|\rangle$$
$$-\langle\!\langle\varphi_0(\mathbf{p})\varphi_0(\mathbf{p}')R(\mathbf{p},\mathbf{p}')\rangle\!\rangle'\langle|v_z|\rangle]$$
$$=\frac{\pi}{2T_c\eta m_{zz}^{-1}}\langle\!\langle[\varphi_0(\mathbf{p})-\varphi_0(\mathbf{p}')]^2R(\mathbf{p},\mathbf{p}')\rangle\!\rangle'\langle|v_z|\rangle. \tag{4.3}$$

As in the limiting cases discussed above, the coefficient α satisfies the condition $\alpha\geqslant 0$; it depends on the orientation of the crystallographic axes with respect to the surface and on the reflection law. It vanishes only in the case of specular reflection, when the reflecting surface coincides with a symmetry plane of the reciprocal lattice. The coefficient α is equal in order of magnitude to the anisotropy parameter of the energy gap divided by the size ξ_0 of a Cooper pair.

APPENDIX

To find the coefficient α, which determines the asymptotic behavior of the solution of Eq. (2.4) at large z, we use a variational principle analogous to that used in calculating phase shifts in a scattering problem. We set

$$\Psi(z)=\Psi_0(z)+\chi(z)=1+\alpha z+\chi(z), \tag{A.1}$$

where $\chi(z)\to 0$ as $z\to\infty$. This function satisfies the inhomogeneous integral equation

$$\hat{K}\chi=-\hat{K}\Psi_0=-\hat{K}1-\alpha\hat{K}z, \tag{A.2}$$

where $\hat{K}$ is an integral operator corresponding to Eq. (2.4), including its left side; i.e., $\hat{K}\Psi=0$. Here is should be noted that

$$\lambda_0/vg=\pi T_c\sum_\omega|\omega|^{-1}=\ln(2\gamma\omega_D/\pi T_c). \tag{A.3}$$

Equation (A.2) follows from a variational principle for the functional

$$J=-(\Psi_0\hat{K}\chi)^2(\chi\hat{K}\chi)^{-1}=[(1\hat{K}\chi)+\alpha(z\hat{K}\chi)]^2(\chi\hat{K}\chi), \tag{A.4}$$

where we have taken into account the fact that operator $\hat{K}$ is self-adjoint.

On the other hand, the value of this functional for the exact solution of Eq. (A.2) is

$$J=-(\Psi_0\hat{K}\Psi_0)=-(1\hat{K}1)-\alpha[(z\hat{K}1)+(1\hat{K}z)]-\alpha^2(z\hat{K}z), \tag{A.5}$$

where, for a diffuse reflection law, we would have

$$(1\hat{K}1)=-[\langle\varphi_0^2(\mathbf{p})|v_z|\rangle-\langle\varphi_0(\mathbf{p})|v_z|\rangle^2\langle|v_z|\rangle^{-1}]\frac{\pi T}{4}\sum_\omega\omega^{-2},$$

$$(z\hat{K}1)+(1\hat{K}z)=\langle\varphi_0(\mathbf{p})|v_z|\rangle\langle\varphi_0(\mathbf{p})v_z^2\rangle$$
$$\times\langle|v_z|\rangle^{-1}\frac{\pi T}{4}\sum_\omega|\omega|^{-3},$$

$$(z\hat{K}z)=[\langle\varphi_0^2(\mathbf{p})|v_z|^3\rangle+\langle\varphi_0(\mathbf{p})v_z^2\rangle^2\langle|v_z|\rangle^{-1}\frac{\pi T}{16}\sum_\omega\omega^{-4}. \tag{A.6}$$

Equating (A.4) and (A.5), we find a quadratic equation

for α, which determines α as a functional of $\chi(z)$. Using a reasonable trial function, e.g., $\chi(z) = \exp(-\beta z)$, we find α by the variational method.

In the case of a slight anisotropy, $(1\hat{K}1)$ is small in units of ξ_0, and α is found to be

$$\alpha = -\frac{(1\hat{K}1)}{(z\hat{K}1)+(1\hat{K}z)} \tag{A.7}$$

and to depend on the trial function only in the next higher order in the anisotropy parameter. Using (A.6) and the analogous expressions for the specular and general reflection laws, we can thus find expressions (2.6), (3.2), and (4.3) for α.

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