Boundary conditions in the macroscopic theory of superconductivity

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This note is devoted to the role played by the boundary conditions in the macroscopic theory of superconductivity. For "usual" superconductors one uses the boundary condition which does not contain any kind of a constant characterizing the superconductor. But in the general case the boundary condition involves a certain length Λ (the extrapolation length). Taking into account of a more general boundary condition may turn out to be significant for high-temperature superconductors in which the coherence length is small.

The present note is of a methodological nature and is devoted to the role played by the boundary conditions of a general form in the macroscopic theory of superconductivity. The choice of such conditions is important in the solution of specific problems—particularly in the case of HTSC (high temperature superconductors).

Within the framework of the well-known macroscopic theory of superconductivity we shall base ourselves on the following expression for the volume free energy of the system:[1–3]

$$F_t=F_{n0}+\int\left[\frac{B^2}{8\pi}+a|\Psi|^2+\frac{b}{2}|\Psi|^4+\frac{1}{4m^*}\left|\left(-i\hbar\nabla-\frac{2e}{c}\mathbf{A}\right)\Psi\right|^2\right]dV, \quad (1)$$

where F_{n0} is the free energy of the normal state, $\mathbf{B}$ is the magnetic induction, $\mathbf{B}=\text{curl}\,\mathbf{A}$, e is the charge of the electron, c is the velocity of light, $\hbar$ is the quantum constant and m^* is a certain mass which one can regard as the mass of the free electron [the point is that the value of the coefficient denoted in (1) by $1/4m^*$, can be chosen arbitrarily in connection with the fact that the magnitude of $|\Psi|^2$ is not fixed[4]]; obviously, in (1) we restrict ourselves to the isotropic case—otherwise the mass tensor with the principal values m_i^* is involved (see, for example, Ref. 3). Further, in (1) a and b are coefficients where b does not depend on T and

$$a=\alpha\frac{T-T_c}{T_c}, \quad (2)$$

where T_c is the critical temperature of the superconducting transition. The equilibrium value of the macroscopic wave function Ψ corresponds to the minimum of F_t and is obtained by solving the system of equations:

$$a\Psi+b|\Psi|^2\Psi+\frac{1}{4m^*}\left(-i\hbar\nabla-\frac{2e}{c}\mathbf{A}\right)^2\Psi=0, \quad (3a)$$

$$\text{curl}\,\mathbf{B}=\frac{4\pi}{c}\mathbf{j}, \quad (3b)$$

$$\mathbf{j}=-\frac{ie\hbar}{2m^*}(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)-\frac{2e^2}{m^*c}|\Psi|^2\mathbf{A}, \quad (3c)$$

where $\mathbf{j}$ is the density of the superconducting current (we assume that the normal current is absent). The boundary conditions for the system of equations (3) reduce to the condition of continuity of all the components of the magnetic induction vector $\mathbf{B}$ at the boundary of the superconductor and to a certain boundary condition for the function Ψ. We shall now undertake the discussion of this latter condition. A number of publications is naturally devoted to the solution of equations (3) using boundary conditions; these questions are discussed also in monographs (see Refs. 4, 5).

In the majority of cases, just as was done from the outset,[1] the boundary conditions

$$\mathbf{n}\left(-\nabla+\frac{2ei}{c\hbar}\mathbf{A}\right)\Psi\Big|_s=0, \quad (4)$$

was used where the subscripts, both here and subsequently, denotes that the value of the quantities is taken on the surface of the superconductor, and $\mathbf{n}$ is the vector of the external normal to the surface.

Condition (4) was obtained in Ref. 1, one can say, automatically from the requirement of looking for the minimum of the variation of the energy F_t with a not fixed value of Ψ on the boundary. In the more general approach condition (4) is obtained below. At the same time, in the macroscopic theory of superfluidity of liquid helium the boundary condition[6] $\Psi_s=0$ was justified and used. Thus, the question arises of the general form of the boundary condition, which, as far as we know, began to be discussed in Ref. 4. Such a more general condition (sometimes called the mixed boundary condition) has the form:

$$\mathbf{n}\left(-\nabla+\frac{2ei}{c\hbar}\mathbf{A}\right)\Psi\Big|_s=\frac{1}{\Lambda}\Psi_s, \quad (5)$$

where Λ is the phenomenological coefficient with the dimensionality of length, sometimes called the extrapolation length. Condition (5) can be obtained on the basis of different considerations, among them taking into account that this most general condition guaranteeing the vanishing of the component of the current density normal to the boundary, i.e., the equation $(\mathbf{nj})=0$. For us, however, the derivation of condition (5) on the basis of the same phenom-

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enological considerations from which equations (3) were obtained is preferable. In this spirit one should add to the functional (1) the surface contribution

$$F_s=F_{s,n}+\int(\gamma|\Psi_s|^2+...)dS, \tag{6}$$

where $F_{s,n}$ is the surface contribution to the free energy for the normal state, and the density of the superconducting free energy is represented in the form of an expansion in powers of Ψ_s of the order parameter on the boundary of the sample. The conditions of applicability of the expansion (6) apparently coincide with the conditions of the applicability of the expansion (1), while such a method itself of taking into account the surface contribution was proposed in Ref. 7, and see also Refs. 3, 8, and 9.

The coefficient γ in (6) can be expressed in terms of the difference in the values of the coefficient a [see (2)] on the surface and in the bulk of the superconductor, or, which is the same thing, in terms of the difference $T_c-T_{c,s}$ of the values of the temperature of the superconducting transition in the bulk of the superconductor T_c and in a certain near-surface layer $T_{c,s}$ which is of thickness of the order of the lattice constant l:

$$\gamma=\frac{al(T_c-T_{c,s})}{T_c}. \tag{7}$$

Condition (5) is obtained if one varies with respect to Ψ^* the total free energy F_t+F_s [see (1) and (6)] as the requirement for the vanishing of the factor multiplying $\delta\Psi^*$. This is accompanied by

$$\Lambda=\frac{\hbar^2}{4m^*\gamma}. \tag{8}$$

Some time ago one also considered the derivation of the boundary condition (5) from the microscopic theory of superconductivity (Refs. 10–13) in the same limiting case

$$\frac{T_c-T}{T_c}\ll 1,\quad \delta(T)\gg\xi(0)$$

$\delta(T)$ is the London penetration depth, $\xi(0)$ is the coherence length at $T=0$ defined below [see (10)] in which the equations (3) themselves are valid (Ref. 14). It was shown that Λ is determined by the properties of the material adjacent to the superconductor. For a boundary with a dielectric in the case of specular reflection of electrons from the boundary,[10] Λ tends to infinity and the boundary condition (4) holds. For a superconductor-normal metal boundary it was shown[11] that $\Lambda\sim\xi(0)$. In this case, Λ may vary in a wide range depending on the parameters of the normal metal. In ordinary (not high-temperature) superconductors the coherence length $\xi(0)$ is quite significant and this provides the possibility of using the boundary condition (4), as is usually done. Indeed, according to (7) and (8) we have

$$\Lambda=\frac{\hbar^2}{4m^*\gamma}=\frac{\hbar^2T_c}{4m^*al(T_c-T_{c,s})}=\frac{\xi^2(0)T_c}{l(T_c-T_{c,s})}, \tag{9}$$

since in the theory of Ref. 1 (see Ref. 3)

$$\xi^2(T)=\left|\frac{\hbar^2}{4m^*a}\right|=\frac{\xi^2(0)T_c}{T_c-T},\qquad \xi^2(0)=\frac{\hbar^2}{4m^*\alpha}. \tag{10}$$

If the length $\xi(0)$ is large (roughly speaking, significantly greater than l), then $\Lambda\gg\xi(0)$, and also the following condition can be satisfied

$$\Lambda\gg\xi(T). \tag{11a}$$

Generally speaking, $\partial\Psi/\partial z\sim\Psi/\xi$ and therefore under the condition (11a) the expression (5) goes over into (4).

In contrast, if

$$\Lambda\ll\xi(T), \tag{11b}$$

then the condition (5) takes on the form

$$\Psi_s=0. \tag{12}$$

In high-temperature superconductors, as is well known (see, for example, Ref. 15), the coherence length $\xi(0)$ is small. Therefore the necessity of using condition (12) is possible or, in any case, one should use the general boundary condition (5) and not the condition (4).

In principle, negative values of the coefficients γ and Λ are possible, and then the boundary facilitates the appearance of superconductivity. This case, apparently, is realized at the boundaries of twins in tin.[16]

The boundary conditions considered above change their form in the case of the boundary of an anisotropic superconductor [see, for example, Ref. 3, where the anisotropy of effective masses is taken into account and also equations (3) are written in differential-difference form for layered superconductors]. Boundary conditions for anisotropic superconductors were specifically examined in Ref. 17, where it was shown that for the boundary superconductor-dielectric γ differs from zero, both for diffuse reflection from the boundary and also for the anisotropic superconductor with an arbitrary orientation of the boundary (for an isotropic superconductor in the case of specular reflection as has already been shown, $\gamma=0$).

Let us study now a chain of problems in which the consideration of more general boundary conditions (5) can be essential for the results being obtained. In doing so, we go over using a standard method to new units, which enable us to free ourselves from the majority of the constants in equations (3). The new quantities are denoted by primes which subsequently are omitted. Thus,

$$\Psi'=\Psi/\Psi_0,\quad \Psi_0^2=-a/b, \tag{13}$$

where Ψ_0 is the equilibrium value of Ψ in a homogeneous superconductor without a magnetic field. Further we have

$$A'=\frac{A}{\sqrt{2}H_c\delta(T)},\quad \delta^2(T)=-\frac{m^*c^2b}{8\pi e^2a},\qquad H_c=-\frac{2a\sqrt{\pi}}{b^{1/2}}, \tag{14}$$

where H_c is the thermodynamic critical field. Finally

$$r' = r/\xi(T), \tag{15}$$

$$\Lambda' = \Lambda/\xi(T). \tag{16}$$

Then equations (3) are brought to the form:

$$-\Psi + |\Psi|^2\Psi + (-i\nabla - \mathbf{A})^2\Psi = 0, \tag{17a}$$

$$\varkappa^2 \text{ curl curl } \mathbf{A} = -\frac{i}{2}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - |\Psi|^2\mathbf{A}, \tag{17b}$$

where $\varkappa = \delta(T)/\xi(T)$ and the boundary condition (5) is

$$\mathbf{n}(-\nabla + i\mathbf{A})\Psi|_s = \frac{1}{\Lambda}\Psi_s. \tag{18}$$

The critical temperature (in the absence of a field) of a thin film of thickness d in the case of the general boundary condition was examined in Ref. 12, see also Refs. 18, 19. We also note Refs. 20–22, in which for the analysis of experimental data on HTSC the solution was used with the limiting variant of (12) for the boundary condition.

The direction perpendicular to the plane of the film is denoted by z with the film occupying the region $0 \leqslant z \leqslant d$. Then equation (17a) has the form

$$d^2\Psi/dz^2 + \Psi - \Psi^3 = 0. \tag{19}$$

Its solution is expressed in terms of the elliptic sine[23]

$$\Psi(z) = \left(\frac{2k^2}{1+k^2}\right)^{1/2} \times \text{sn}\left(\frac{z-(d/2)}{(1+k^2)^{1/2}} + K, k\right), \tag{20}$$

where k is the modulus determined from the transcendental equation which follows from (18);

$$1 - (1+k^2)\left(1 + \frac{1}{\Lambda^2}\right)y^2 + k^2y^4 = 0;$$
$$y = \text{sn}\left(-\frac{d}{2(1+k^2)^{1/2}} + K, k\right), \tag{21}$$

K is the complete elliptic integral of the first kind

$$K \equiv K(k) = \int_0^{\pi/2} \frac{d\varphi}{(1-k^2\sin^2\varphi)^{1/2}}.$$

Equation (21) defines k as an implicit function of d and Λ and also of the temperature T [since d and Λ are expressed in the units of (15)]; it can be brought to the form[23]

$$\text{tg}\, x = \frac{d}{x\Lambda} - 4\sum_{n=1}^{\infty}(-1)^n \frac{\sin(nx)}{e^{nW}-1}, \tag{22}$$

where

$$x = \frac{\pi d}{2(1+k^2)^{1/2}K},$$

$$W = \frac{\pi K'}{K},$$

K' is the elliptic integral of the additional modulus $k' = (1-k^2)^{1/2}$.

The disappearance of superconductivity in the film [appearance of the solution of (20) with a zero amplitude] corresponds to the temperature $T_c^*(d,\Lambda)$ at which k becomes zero. In order to determine T_c^* in the zero-order approximation one can omit the second term in the right-hand side of (22) and to obtain in the limiting cases

$$T_c^*(d,\Lambda) = T_c\left(1 - \frac{\pi^2\xi^2(0)}{4d^2}\right), \quad \Lambda \ll d, \tag{23a}$$

$$= T_c\left(1 - \frac{\xi^2(0)}{d\Lambda}\right), \quad \Lambda \gg d, \tag{23b}$$

where d and Λ are now shown in unreduced units.

The equation $T_c^*(d,\Lambda) = T$ determines the critical thickness $d_c(T)$ of the film;[6,12] as the thickness d is decreased at a given temperature T the temperature of the transition falls and at $d = d_c(T)$ the superconductivity in the film vanishes; this is accompanied by $\Psi(z) = 0$, which corresponds to $k = 0$ and the elliptic sine becomes $\text{sn}\, x = \sin x$. Consequently from the boundary condition (18) we obtain

$$d_c(T) = 2\xi(T)\,\text{arctg}\,\frac{\xi(T)}{\Lambda}. \tag{24}$$

In the limiting case (11a), which corresponds to the usually employed boundary condition (4), it is evident that $d_c(T) = 0$, i.e., superconductivity of the film within the framework of the macroscopic theory always exists. In the opposite limiting case (11b) which corresponds to the boundary condition (12), we have

$$d_c(T) = \pi\xi(T)$$

(this formula is the one that was obtained in Ref. 6 for liquid helium).

In Ref. 18 a calculation was made also of the discontinuity of the heat capacity of the film at the moment of the transition at $T = T_c^*(d,\Lambda)$ for an arbitrary value of d/Λ

$$\Delta C = \tfrac{2}{3}\Delta C_0 \times \frac{\left(1 + \frac{\sin u}{u}\right)^2}{1 + \frac{\sin u}{u}\left(1 + \frac{2}{3}\cos^2\frac{u}{2}\right)}, \tag{25}$$

where ΔC_0 is the discontinuity in the heat capacity in a massive superconductor and the parameter $u = 2d/\xi(T_c^*)$, $\xi^2(T_c) = \hbar^2 T_c$ and $/4m^*\alpha(T_c - T_c^*(d,\Lambda))$. For $u = 2(d/\Lambda)^{1/2} \ll 1$ the suppression of superconductivity at the boundary of the film is relatively not very great, $\Delta C = \Delta C_0$. In the opposite limiting case $\Lambda \ll d$ the parameter $u = \pi$ and the discontinuity in the specific heat capacity amounts to $(2/3)\Delta C_0$.

In Ref. 18 a discussion was given also of the magnetic susceptibility of thin films near T_c^* in a weak field parallel to the surface of the film. In particular, on the assumption that $\varkappa \gg 1$ and that the magnetic field is so weak that it does not affect in the zero-order approximation the amplitude Ψ the following formula for the susceptibility was obtained:

$$\chi(T) = -\frac{1}{48\pi}\frac{d^2}{\delta^2(T_c^*)}\varphi(u)\frac{T_c^* - T}{T_c - T_c^*}, \tag{26}$$

where

$$\varphi(u)=\frac{\left(1+\frac{3\sin u}{u^3}-\frac{3\cos u}{u^2}\right)(u+\sin u)}{1.5u+\sin u\left(1.5+\cos^2\frac{u}{2}\right)}.$$

Thus, in the case $d\sim\xi(T_c^*)\gg\xi(0)$, Λ one can expect some differences of the thermodynamic quantities in the field near the superconducting transition from the usual ones.

The form of the boundary condition also exerts a considerable influence on the solution of the problem concerning the appearance of a superconducting nucleus near the surface of the superconductor as the magnetic field is decreased. As was shown in Ref. 24 (see also Ref. 4) in the case of the boundary condition (4) in a field parallel to the surface of the sample surface superconductivity arises at a field intensity $H\leqslant H_{c3}\approx 1.7H_{c2}$. Taking into account a more general boundary condition or, what is the same, an additional surface energy (6) changes the conditions for the formation of superconducting nuclei. As has been shown in Ref. 13 as $\gamma\to\infty$ (i.e., $\Lambda\to 0$) the field $H_{c3}\to H_{c2}$, i.e., surface superconductivity is suppressed. The converse situation, generally speaking, can be expected for negative γ, however, it is not very clear how one can create the free surface characterized by such a phenomenological parameter.

Above we considered the order parameter (the function Ψ to be a complex scalar, i.e., we had in mind the so-called *s*-pairing. One must remember, however, that also a more general pairing is possible, for which the order parameter is the function Ψ of a more complex form (see, for example, Ref. 25). Naturally, the problem of boundary conditions exists also in the case of a more general pairing and must be solved taking into account the nature of the order parameter.

In a number of cases it turns out to be necessary to calculate the fluctuations of the different quantities and, in particular, the fluctuation corrections to the heat capacity (see, for example, Ref. 3; as is well known, the role played by the fluctuations is particularly great for high-temperature superconductors). In solving the corresponding problems one should utilize definite boundary conditions for Ψ. This set of problems, as far as we know, has not yet been investigated. Apparently, taking into account a more general boundary condition is needed for the interpretation of experiments on the diffraction of low-energy electrons on the surface. The same can, generally speaking, be said concerning the analysis of the role played by the boundary conditions that appears to be very necessary from the point of view of the interpretation of some other experiments with high-temperature superconductors. This is in fact the explanation of our attention to the problem of boundary conditions raised in the present note.

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