6

# On the Theory of Superconductivity †

The existing phenomenological theory of superconductivity is unsatisfactory since it does not allow us to determine the surface tension at the boundary between the normal and the superconducting phases and does not allow for the possibility to describe correctly the destruction of superconductivity by a magnetic field or current. In the present paper a theory is constructed which is free from these faults. We find equations for the Ψ-function of the "superconducting electrons" which we introduced and for the vector potential. We have solved these equations for the one-dimensional case (a superconducting half-space and flat plates).

The theory makes it possible to express the surface tension in terms of the critical magnetic field and the penetration depth of the magnetic field in superconductors. The penetration depth depends in a strong field on the field strength and this effect will be especially evident in the case of small size superconductors. The destruction of superconductivity in thin plates by a magnetic field is through a second-order phase transition and it only becomes a first-order transition starting with plates of a thickness more than a certain critical thickness. While the critical external magnetic field increases with decreasing thickness of the plates, the critical current for destroying the superconductivity of plates decreases with decreasing thickness.

## Introduction

It is well known that there exists at present no properly developed microscopic theory of superconductivity. At the same time there is a fairly widespread view that the phenomenological theory of superconductivity is in a much more satisfactory state and is reliably based on the equation of F. and H. London[1, 2]:

$$\operatorname{curl} \Lambda \boldsymbol{j}_s = -\frac{1}{c} \boldsymbol{H}, \tag{1}$$

† With V. L. Ginzburg, *J. Exptl. Theoret. Phys.* (*USSR*), **20**, 1064, 1950.





where $\Lambda$ is a quantity depending only on temperature, $\boldsymbol{j}_s$ is the supercurrent density, $c$ is the velocity of light and $\boldsymbol{H}$ is the magnetic field strength, here identical with the magnetic induction. Equation (1) in combination with Maxwell's equation, $\operatorname{curl} \boldsymbol{H} = 4\pi \boldsymbol{j}_s/c$, and the equations $\operatorname{div} \boldsymbol{H} = 0$ and $\operatorname{div} \boldsymbol{j}_s = 0$, leads under stationary conditions to the equations:

$$\nabla^2 \boldsymbol{H} - \boldsymbol{H}/\delta^2 = 0 \text{ and } \nabla^2 \boldsymbol{j}_s - \boldsymbol{j}_s/\delta^2 = 0, \text{ where } \delta^2 = \Lambda c^2/4\pi. \tag{2}$$

For a plane boundary between the superconductor and vacuum or a non-superconductor these equations have solutions:

$$H = H_0 e^{-z/\delta} \text{ and } j_s = \frac{c}{4\pi\delta} H, \tag{3}$$

in which the external field $H_0$ is taken as parallel to the boundary, which is normal to the $z$-axis. For a film of thickness $2d$ in a parallel field we get:

$$H = H_0 \cosh (z/\delta)/\cosh (d/\delta),$$
$$j_s = -\frac{cH_0}{4\pi\delta} \sinh (z/\delta)/\cosh (d/\delta), \tag{4}$$

if $z = 0$ at the centre of the film.

For a superconductor of arbitrary shape it follows from (2) that the field penetrates only to a depth of the order of $\delta$, which is according to experimental data about $10^{-5}$ cm. Qualitatively, this result is, of course, in agreement with the fact that a magnetic field does not penetrate into the body of a superconductor; quantitatively, however, there is no certainty that equations (1) to (4) are always correct. Moreover, this theory throws no light on the question of the surface energy at a boundary between superconducting and normal phases of the same metal, and also leads to a contradiction with experiment concerning the destruction of superconductivity of a thin film by a magnetic field.

The thermodynamic treatment of the transition of a film of thickness $2d$ from the superconducting to the normal state leads[2, 3] to the following expression for the critical field, $H_c$:

$$\left(\frac{H_c}{H_{cb}}\right)^2 = \left(1 - \frac{\delta}{d} \tanh \frac{d}{\delta}\right)^{-1} \tag{5}$$

in which $H_{cb}$ is the critical field of the bulk material. This expression is not in agreement with experiment. Thus, if at a given temperature the constant $\delta$ is determined from measured values of $(H_c/H_{cb})^2$ for various values of $d$, according to (5), then this "constant" $\delta$ depends markedly on $d$; for example, if $T = 4°$ then for $d = 0{\cdot}3 \times 10^{-5}$ cm, $\delta = 3{\cdot}4 \times 10^{-5}$ cm, while for $d = 1{\cdot}2 \times 10^{-5}$ cm, $\delta = 2 \times 10^{-5}$ cm.

It has been pointed out[3] that the position may be improved by taking into account the difference of the surface energy at the boundary of the metal with a vacuum according as the metal is in the superconducting or the normal state; the difference of surface energies, $\sigma_s - \sigma_n$, introduced for this purpose must be of the order of $\delta H_{cb}^2/8\pi$. Now the surface energy is usually equal to the bulk free energy per unit volume times a length of the order of atomic dimensions. Thus here, where the difference of free energies is $H_{cb}^2/8\pi$, one might expect $\sigma_s - \sigma_n$ to be of the order of $10^{-7}$ to $10^{-8}$ times $H_{cb}^2/8\pi$ and not $10^{-5}$ $H_{cb}^2/8\pi$. An even more contradictory situation arises at the boundary separating the normal and superconducting phases of the metal; the surface energy connected with the field and supercurrent here as predicted from the solution of equation (3), is equal[5, 3] to $-\delta H_{cb}^2/8\pi$, i.e., is negative. Thus in order to obtain the observed positive surface energy $\sigma_{ns}$, it is necessary to introduce a surface energy, $\sigma'_{ns}$, of non-magnetic origin, which is given by the equation:

$$\sigma'_{ns} = \sigma_{ns} + \frac{\delta H^2}{8\pi}$$

and which is greater than $\delta H_{cb}^2/8\pi$. There is no justification for introducing such a relatively enormous energy $\sigma'_{ns}$ not connected with the field distribution. On the contrary one would expect any rational theory of superconductivity to lead automatically to an expression for $\sigma'_{ns}$ in terms of the ordinary parameters characterising the superconductor.

The theory based on equation (1), even with the additional surface energy, does not enable the destruction of superconductivity in thin films by a current[6] to be considered, since this problem is not of a thermodynamic nature.



The aim of the present work is the construction of a theory free from these defects. Incidentally, as we shall see, the theory leads also to a number of new qualitative conclusions which may be checked experimentally.

## 1. Basic Equations

In the absence of a magnetic field the transition into the superconducting state at the critical temperature $T_c$ is a phase transition of the second kind. In the general theory of such transitions[7] there always enters some parameter $\eta$ which differs from zero in the ordered phase and which equals zero in the disordered phase. For example, in ferroelectrics the spontaneous polarisation plays the role of $\eta$ and in ferromagnetics the spontaneous magnetisation[8]. In the phenomenon of superconductivity, in which it is the superconducting phase that is ordered, we shall use $\Psi$ to denote this characteristic parameter. For temperatures above $T_c$, $\Psi = 0$ in the state of thermodynamic equilibrium, while for temperatures below $T_c$, $\Psi \neq 0$. We shall start from the idea that $\Psi$ represents some "effective" wave function of the "superconducting electrons". Consequently $\Psi$ may be precisely determined only apart from a phase constant. Thus all the observable quantities must depend on $\Psi$ and $\Psi^*$ in such a way that they are unchanged when $\Psi$ is multiplied by a constant of the type $e^{i\alpha}$. We may note also that since the quantum mechanical connection between $\Psi$ and the observable quantities has not yet been determined we may normalize $\Psi$ in an arbitrary manner. We shall see below how we must carry out this normalisation in such a way that $|\Psi|^2$ shall equal the concentration, $n_s$, of "superconducting electrons" introduced in the usual way.

Consider first a uniform superconductor in the absence of a magnetic field, and suppose that $\Psi$ is independent of position. The free energy of the superconductor is then in accordance with the general theory of second-order phase transitions, dependent only on $|\Psi|^2$ and may be expanded in series form in the neighbourhood of $T_c$. Thus near $T_c$ we may write for the free energy $F_{so}$,

$$F_{so} = F_{no} + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4. \qquad (6)$$

In equilibrium

$$\frac{\partial F_{so}}{\partial|\Psi|^2} = 0, \quad \frac{\partial^2 F_{so}}{\partial^2|\Psi|^2} > 0,$$

and in addition we must have that $|\Psi|^2 = 0$ for $T \geqq T_c$ and $|\Psi|^2 > 0$ for $T > T_c$. It follows therefore that $\alpha_c = 0$, $\beta_c > 0$, and for $T < T_c$, $\alpha < 0$. Thus in equilibrium, for $T \leqq T_c$,

$$|\Psi|^2 = |\Psi_\infty|^2 = -\frac{\alpha}{\beta} = \frac{T_c - T}{\beta_c}\left(\frac{d\alpha}{dT}\right)_c,$$

and

$$F_{so} = F_{no} - \frac{\alpha^2}{\alpha\beta} = F_{no} - \frac{(T_c - T)^2}{2\beta_c}\left(\frac{d\alpha}{dT}\right)_c^2, \tag{7}$$

in which it is taken into account that, within the limits of validity of the expansion (6), $\alpha(T) = (d\alpha/dT)_c(T_c - T)$ and $\beta(T) = \beta_c$; the choice of the subscript $\infty$ for $\Psi$ is determined by considerations of convenience which will become evident from what follows. The quantity $F_{no}$ in (6) and (7) is evidently the free energy of the normal phase. Well-known thermodynamic considerations show (see also below) that $F_{so} - F_{no} = H_{cb}^2/8\pi$, where $H_{cb}$ is the critical magnetic field for a bulk specimen and the free energies, as everywhere in this paper, relate to unit volume. Thus from (7),

$$H_{cb}^2 = \frac{4\pi\alpha^2}{\beta} = \frac{4\pi(T_c - T)^2}{\beta_c}\left(\frac{d\alpha}{dT}\right)_c^2. \tag{8}$$

The form of this expression is well known to be completely confirmed by experiment, which therefore provides a foundation for the assumptions made above.

Consider now a superconductor in a time-independent magnetic field. In order to obtain the density of total free energy $F_{sH}$, it is now necessary to add to $F_{so}$ the field energy $H^2/8\pi$ and the energy connected with the possible appearance of a gradient of $\Psi$ in the presence of a field. This last energy, at least for small values of $|\text{grad}\ \Psi|^2$, can as a result of series expansion with respect to $|\text{grad}\ \Psi|^2$ be expressed in the form const $|\text{grad}\ \Psi|^2$, i.e., it looks like a kinetic



energy density in quantum mechanics. Thus we shall write the corresponding expression in the form

$$\left(\frac{\hbar^2}{2m}\right)|\text{grad}\ \Psi|^2 = \frac{1}{2m}\,|-i\hbar\ \text{grad}\ \Psi|^2$$

in which $\hbar$ (= $1{\cdot}05 \times 10^{-27}$ gcm$^2$ sec$^{-1}$) is Dirac's constant and $m$ is a certain coefficient. We have not, however, taken into account as yet the interaction between the magnetic field and the current connected with the presence of grad $\Psi$. In view of what has been said, and the requirement that the whole scheme shall be gauge-invariant, we must allow for the influence of the field by making the usual change of $-i\hbar$ grad to $(-i\hbar\ \text{grad} - eA/c)$, where $A$ is the vector potential of the field and $e$ is a charge, which there is no reason to consider as different from the electronic charge. Thus the energy density connected with the presence of grad $\Psi$ and the field $H$ takes the form

$$\frac{H^2}{8\pi} + \frac{1}{2m}\left|-i\hbar\ \text{grad}\ \Psi - \frac{e}{c}A\Psi\right|^2.$$

Consequently

$$F_{sH} = F_{sn} + \frac{H^2}{8\pi} + \frac{1}{2m}\left|-i\hbar\ \text{grad}\ \Psi - \frac{e}{c}A\Psi\right|^2. \tag{9}$$

The equation for $\Psi$ may now be found from the requirement that the total free energy of the body, $\int F_{sH}dV$, shall be as small as possible. Thus, varying with respect to $\partial\Psi$, we find that

$$\frac{1}{2m}\left(-i\hbar\ \text{grad} - \frac{e}{c}A\right)^2\Psi + \frac{\partial F_{s0}}{\partial\Psi^*} = 0 \tag{10}$$

and moreover, at the boundary of the superconductor, in view of the arbitrariness of the variation $\delta\Psi^*$, the following condition must hold:

$$\left(\boldsymbol{n}\cdot\left[-i\hbar\ \text{grad}\ \Psi - \frac{e}{c}A\Psi\right]\right) = 0, \tag{11}$$

where $\boldsymbol{n}$ is the unit vector normal to the boundary.

The condition (11) is obtained if no supplementary requirements are imposed on $\Psi$ (natural boundary conditions); if however it is demanded from the start that at the boundary with a vacuum $\Psi = 0$ then (11) is not obtained. But the condition $\Psi = 0$ or const is not admissible in the present scheme, since then there would be no solution to the problem of the superconducting plate except for particular values of the thickness $2d$. We therefore impose no further conditions on $\Psi$ at the boundary with a vacuum, and are thus led to (11). At first sight this result may appear unacceptable, since it is natural to demand that the wave function at the boundary of a metal should vanish. The essence of the matter, however, lies in the fact that the $\Psi$-function introduced above is in no way a true wave function of the electrons in the metal, but is a certain average quantity.

We may suppose that our function $\Psi(\boldsymbol{r})$ is directly connected with the density-matrix $\rho(\boldsymbol{r}, \boldsymbol{r}') = \int \Psi(\boldsymbol{r}, \boldsymbol{r}_i')\Psi(\boldsymbol{r}', \boldsymbol{r}_i')d\boldsymbol{r}_i'$, where $\Psi(\boldsymbol{r}, \boldsymbol{r}_i')$ is the true wave-function of the electrons in the metal, depending on the coordinates of all electrons, $\boldsymbol{r}_i (i = 1, 2, \ldots N)$; the $\boldsymbol{r}_i'$ are the coordinates of all the electrons except the one considered, whose coordinates at two points are taken as $\boldsymbol{r}$ and $\boldsymbol{r}'$. It might be thought that when $|\boldsymbol{r} - \boldsymbol{r}'| \to \infty$, $\rho = 0$ for a non-superconducting body having no long-range order, while in the superconducting state $\rho = \rho_0 (\neq 0)$. It is reasonable to suppose now that the density-matrix is connected with our $\Psi$-function by the relation $\rho(\boldsymbol{r}, \boldsymbol{r}') = \Psi^*(\boldsymbol{r})\Psi(\boldsymbol{r}')$.

So far as the equation for $A$ is concerned, if we assume that $\operatorname{div} A = 0$ and vary the free energy with respect to $A$ we obtain the usual expression:

$$\nabla^2 A = -\frac{4\pi}{c} j = \frac{2\pi i e\hbar}{mc}(\Psi^* \operatorname{grad}\Psi - \Psi \operatorname{grad}\Psi^*) + \frac{4\pi e^2}{mc^2}|\Psi|^2 A, \tag{12}$$

in which the right-hand side contains the expression for the supercurrent:

$$j = -\frac{ie\hbar}{2m}(\Psi^* \operatorname{grad}\Psi - \Psi \operatorname{grad}\Psi^*) - \frac{e^2}{mc}\Psi^*\Psi A.$$



It should be noticed that an expression analogous to (11) is obtained for the quantity in brackets, from which it is evident that at the boundary $(\boldsymbol{j} \cdot \boldsymbol{n}) = 0$, as required. The solution of the problem of the distribution of field and current in a superconductor is now reduced to an appropriate integration of equations (10) and (12).

We shall examine below only the one-dimensional problem, with the $z$-axis normal to the boundary separating the superconducting phase ($z > 0$) from the normal phase or vacuum; we shall take the field $\boldsymbol{H}$ as directed along the $y$-axis and the current $\boldsymbol{j}$ and vector potential $A$ along the $x$-axis (thus $H_y = dA_x/dz$, or simply $H = dA/dz$). In the one-dimensional solution it is natural to consider $|\Psi|^2$ as dependent only $z$, so that $\Psi = e^{i\phi(x,y)}\Psi(z)$. However, bearing in mind the gauge-invariance of the equations, we may by a suitable choice of $A$ arrange that $\Psi = \Psi(z)$ and hence $j = -(e^2/mc)|\Psi|^2 A$ (from the conditions that $\operatorname{div}\boldsymbol{j} = dj/dz = 0$ and $(\boldsymbol{j} \cdot \boldsymbol{n}) = 0$ it follows that $j_z = 0$). Moreover the equations do not now contain the imaginary $i$ (since $(A \cdot \operatorname{grad}\Psi) = (A\boldsymbol{i} \cdot (d\Psi/dz)\boldsymbol{k}) = 0$), and we may therefore consider $\Psi$ as real. Consequently equations (10) and (12) take the form:

$$\frac{d^2\Psi}{dz^2} + \frac{2m}{\hbar^2}|\alpha|\left(1 - \frac{e^2}{2mc^2|\alpha|}A^2\right)\Psi - \frac{2m}{\hbar^2}\beta\Psi^3 = 0,$$

$$\frac{d^2 A}{dz^2} - \frac{4\pi e^2}{mc^2}\Psi^2 A = 0 \tag{13}$$

in which equation (6) has been used, with the additional fact that $\alpha > 0$.

Let us now determine the surface energy at a plane boundary between the normal and superconducting phases. In the normal phase, the total free energy, including field energy, is $F_{n0} + (H_{cb}^2/8\pi)$. In the region where $\Psi \neq 0$ and there is superconductivity the energy density is $F_{sH}$ (equation 9), and in addition we must take account of the energy density due to the " magnetisation " of a superconductor in a field parallel to the boundary with the non-superconducting phase, in the form:

$$-MH_{cb} = -\frac{H(z) - H_{cb}}{4\pi} \cdot H_{cb},$$

where $M$ plays the role of the magnetisation. Thus the surface energy may be written:

$$\sigma_{ns} = \int \left( F_{sH}(z) - \frac{H(z)H_{cb}}{4\pi} + \frac{H_{cb}^2}{4\pi} - F_{no} - \frac{H_{cb}^2}{8\pi} \right) dz, \quad (14)$$

in which the integration is extended over the transition layer between the phases (the $z$-axis is normal to this layer). It is readily verified that the integrand vanishes at great distances from the transition layer, for in the superconducting phase $H = 0$ and $F_{sH} = F_{so} = F_{no} - \alpha^2/2\beta$ (see equation (7)), while in the normal phase, $\Psi = 0$, $F_{sH} = F_{no} + H_{cb}^2/8\pi$ and $H_o = H_{cb}$. From equations (7)–(9),

$$\sigma_{ns} = \int \left\{ \alpha\Psi^2 + \frac{\beta\Psi^4}{2} + \frac{\alpha^2}{2\beta} + \frac{\hbar^2}{2m}\left(\frac{d\Psi}{dz}\right)^2 + \frac{e^2}{2mc^2} A^2\Psi^2 + \frac{H^2}{8\pi} - \frac{H_{cb}H}{4\pi} \right\} dz. \quad (15)$$

From the minimum condition for $\sigma_{ns}$, which is the free energy per unit area, we may of course obtain both the first of equations (13), by variation of (15) with respect to $\Psi$, and the second of equations (13), by variation with respect to $A$.

At the boundary of a superconductor with a vacuum in the one-dimensional case the condition (11) assumes the form

$$\frac{d\Psi}{dz} = 0. \quad (16)$$

We shall now introduce the following parameters, $H_{cb}$, $\delta_0$ and $\kappa$ and in addition new variables, $z'$, $\Psi'$, $A'$ and $H'$:

$$z' = z/\delta_0, \Psi'^2 = \frac{\Psi^2}{\Psi_\infty^2} = \frac{\Psi^2}{|\alpha|/\beta}, A' = \sqrt{\frac{e^2}{2mc^2|\alpha|}} \cdot A = \frac{A}{\sqrt{2}H_{cb}\delta_0},$$

$$H' = \frac{dA'}{dz'} = \frac{1}{\sqrt{2}} \cdot \frac{H}{H_{cb}}, \delta_0^2 = \frac{mc^2\beta}{4\pi e^2|\alpha|} = \frac{mc^2}{4\pi e^2\Psi_\infty^2}, \quad (17)$$

$$H_{cb}^2 = \frac{4\pi\alpha^2}{\beta}, \kappa^2 = \frac{1}{2\pi}\left(\frac{mc}{e\hbar}\right)^2\beta = \frac{2e^2}{\hbar^2c^2} H_{cb}^2\delta_0^4.$$



Equations (13) now take the form:

$$\frac{d^2\Psi}{dz^2} = \kappa^2[-(1 - A^2)\Psi + \Psi^3],$$

$$\frac{d^2A}{dz^2} = \Psi^2A. \quad (18)$$

The primes have been omitted from these equations since in what follows unless we explicitly state the contrary, only the new variables will be used. With these variables, (15) must be written in the form:

$$\sigma_{ns} = \frac{H_{cb}^2}{4\pi}\delta_0 \int \left\{ \tfrac{1}{2} - (1 - A^2)\Psi^2 + \tfrac{1}{2}\Psi^4 + \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 + \left(\frac{dA}{dz}\right)^2 - 2\left(\frac{dA}{dz}\right)_c\left(\frac{dA}{dz}\right) \right\} dz. \quad (19)$$

If $\kappa = 0$, then from (18) and (16) $\Psi^2 = n_s$ = constant, and our equations go over into equations (2) with $\delta^2 = \delta_0^2 = mc^2/4\pi e^2 n_s$ (compare equation (2) with the second of equations (13)). This result is true in general; if we put grad $\Psi = 0$ in equation (12) it becomes equivalent to equation (2), or, more directly, $\boldsymbol{j} = -(e^2/mc)|\Psi|^2A$, which leads to equation (1). Although for $\kappa = 0$ our scheme becomes formally identical with the usual theory, it is substantially different even in this limiting case. For, in equations (1) and (2) the parameter $\Lambda(=4\pi\delta^2/c^2 = m/n_s e^2)$ is a constant, independent of field, at a given temperature, while in our theory, even for $\kappa = 0$, the value of $\Psi^2$ which is the same as $n_s$ and which determines, as in equation (20), the value of $\delta$, is such as to minimise the free energy, and this results in a variation of the penetration depth $\delta$ with $H$ in superconductors of small dimensions.

From the limiting case, $\kappa = 0$, and from the following discussion it is clear that the experimentally determined quantity is the parameter $\delta_0^2(= mc^2/4\pi e^2\Psi_\infty^2)$, $\delta_0$ being the penetration depth for a weak field into a bulk superconductor. It is just this quantity which enters also into the expression for the dielectric constant $\varepsilon(= \varepsilon_0 - 4\pi e^2\Psi_\infty^2/m\omega^2)$ of a superconductor in an alternating field of not too high a frequency $\omega$ ($\varepsilon_0$ is a certain constant contribution to $\varepsilon$ from all particles other than "superconducting electrons").

The parameter $\Psi_\infty^2 (= n_s)$, which evidently corresponds to the concentration of "superconducting electrons", does not appear as a measurable quantity, resembling in this way the number of free electrons in the ordinary quantum theory of metals. Thus in both expressions we may talk only of the effective number of electrons, which may be determined from the values $\varepsilon$ or $\delta_0^2$ by attributing to $m$ the value appropriate to a free electron. Proceeding in this way we relate the concentration of "superconducting electrons" $n_s (= \Psi_\infty^2)$ with the observable quantity $\delta_0$ (putting $e = 4{\cdot}8 \times 10^{-10}$ esu, $m = 9{\cdot}1 \times 10^{-28}$ g) by the equation:

$$\delta_0^2 = \frac{mc^2\beta}{4\pi e^2|\alpha|} = 2{\cdot}84 \times 10^{11}\frac{\beta}{|\alpha|} = \frac{2{\cdot}84 \times 10^{11}}{\Psi_\infty^2}\ \mathrm{cm}^2. \tag{20}$$

From (20) and from measurements of the critical field $H_{cb}$ $(= \sqrt{4\pi\alpha^2\beta})$ we may determine $\alpha$ and $\beta$. Besides $H_{cb}$ and $\delta_0$ (or $\alpha$ and $\beta$) there enters also into the theory the dimensionless parameter $\kappa$:

$$\kappa^2 = \left(\frac{2e^2}{\hbar^2c^2}\right)H_{cb}^2\delta_0^4, \tag{21}$$

which, with $e = 4{\cdot}8 \times 10^{-10}$ esu, becomes:

$$\kappa^2 = 4{\cdot}64 \times 10^{14} H_{cb}^2\delta_0^4, \tag{22}$$

where $\delta_0$ is measured in centimetres and $H_{cb}$ in gauss. From the experimental data discussed in section 4 it follows that for mercury

$$\kappa^2 \doteqdot 0{\cdot}027;\quad \kappa \doteqdot 0{\cdot}165;\quad \sqrt{\kappa} \doteqdot 0{\cdot}406. \tag{23}$$

## 2. The Superconducting Half-space

We shall consider first the case of a superconducting half-space bounded by a vacuum (superconducting for $z > 0$, boundary at $z = 0$). The solution will of course refer also to a sufficiently thick plate whose half thickness $d \gg 1$ (or in the usual units $d \gg \delta_0$). For $z = 0$, $H = H_0$, and for $z = \infty$, $H = A = 0$ (the present choice of $A(\infty) = 0$ is perfectly natural and moreover possible). Further, for $z = \infty$ we are dealing with a superconductor in the absence of a field and far from any boundaries, and consequently solution (7) must apply, i.e., in the new variables $\Psi_\infty^2 = 1$, $d\Psi/dz = 0$. Thus for $z = \infty$,



$$\Psi_\infty^2 = 1,\ \frac{d\Psi}{dz} = H = A = 0. \tag{24}$$

This solution naturally satisfies the equations (18). As regards the boundary with the vacuum at $z = 0$, condition (16) must be satisfied there; substituting (18) into (24) we see that in the absence of a magnetic field the presence of the boundary has no influence on the function $\Psi$ which therefore has the same value everywhere:

$$\Psi^2 = \Psi_\infty^2 = 1 \text{ if } H \equiv A \equiv 0. \tag{25}$$

In the presence of a magnetic field solution (25) of course does not apply and we must integrate (18) with the boundary conditions (24) for $z = \infty$ and the conditions

$$H = \frac{dA}{dz} = H_0,\ \frac{d\Psi}{dz} = 0 \text{ for } z = 0. \tag{26}$$

The values of $A_0$ and $\Psi_0$ are not known beforehand.

The equations (18) unfortunately cannot be integrated exactly and we can indicate only one of their integrals:

$$(1 - A^2)\Psi^2 - \tfrac{1}{2}\Psi^4 + \left(\frac{dA}{dz}\right)^2 + \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 = \text{const.} \tag{27}$$

For the case which interests us the constant is equal to $\frac{1}{2}$ because of (24), and thus

$$H^2 = \left(\frac{dA}{dz}\right)^2 = \tfrac{1}{2} - \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 - (1 - A^2)\Psi^2 + \tfrac{1}{2}\Psi^4. \tag{28}$$

Turning instead to the approximate solution of equations (18), we now give the solution valid for small values of $\kappa$ (more precisely the solution will be valid for small values of the product $\kappa H_0^2$). In order to find this solution we substitute

$$\Psi = \Psi_\infty + \phi = 1 + \phi \text{ for } |\phi| \ll 1. \tag{29}$$

Then in the first approximation up to terms of order $\phi A$ and $\phi^2$, the system (18) assumes the form

$$\frac{d^2\phi}{dz^2} = \kappa^2(2\phi + A^2), \quad \frac{d^2A}{dz^2} = A. \tag{30}$$

This system may be integrated at once and its solution may be used for finding the next approximation and so on. The corresponding solution, with the conditions (24) and (26), up to and including terms in $H_0^3$ has the form

$$\Psi = 1 + \frac{\kappa H_0^2}{\sqrt{2}(2-\kappa^2)}\left(\frac{\kappa}{\sqrt{2}}e^{-2z} - e^{-\kappa z\sqrt{2}}\right),$$

$$A = -H_0e^{-z} - \frac{\kappa H_0^3}{\sqrt{2}(2-\kappa^2)}\left\{\frac{\kappa}{4\sqrt{2}}e^{-3z} - \frac{e^{-(\sqrt{2}\kappa+1)z}}{\kappa(\kappa+\sqrt{2})} - \frac{3\kappa^3 + 3\sqrt{2}\kappa^2 - 8\kappa - 4\sqrt{2}}{4\sqrt{2}\kappa(\kappa+\sqrt{2})}e^{-z}\right\}. \tag{31}$$

For $z = 0$, naturally, $d\Psi/dz = 0$, $H = H_0$ and

$$\Psi_0 = 1 - \frac{\kappa H_0^2}{2(\kappa+\sqrt{2})},$$

$$A_0 = -H_0 - \frac{\kappa(\kappa+2\sqrt{2})}{4(\kappa+\sqrt{2})^2}H_0^3. \tag{32}$$

The biggest of the terms in $\Psi$ neglected in (32) are of the order $\kappa^2H_0^4$ and in $A$ of the order $\kappa^2H_0^5$. The field $H_0$ in the equilibrium state is less than or equal to the critical field $H_{cb}$ for the superconductor, which in the new variables is $1/\sqrt{2}$ (see (17)). According to (32), for $\kappa = 0{\cdot}165$ (see (23)) $\Psi_0 \geqq 0{\cdot}974$ (the equality applies when $H_0 = 1/\sqrt{2}$), and thus the application of equation (31) here is completely justified if it is sufficient to determine $(\Psi - 1)$ to a few per cent.

At the present time such an accuracy in the measurement of $\delta_0$ is far from having been reached.

Since from the experimental data it follows that $\kappa \ll 1$, and also for a reason indicated below the solution of equations (18) possible for another limiting case when $\kappa \to \infty$ does not offer any intrinsic interest, we shall not discuss it.

If $\kappa = 0$, then in the problem under discussion $\Psi \equiv 1$ for any $H$—this corresponds to the usual theory based on equations (1)



with $\Lambda$ = const. If $\kappa > 0$, the solution exists only up to a certain "second critical field" $H_{c2}$. The range of fields $H_{cb}(= 1/\sqrt{2}) < H < H_{cb2}$ represents a metastable (superheated) state in which the superconducting phase can exist since it represents a relative minimum of the free energy but the absolute minimum of free energy is already that corresponding to the normal phase. The more detailed investigation of this question and a calculation of the dependence of the field $H_{c2}$ on $\kappa$ has not yet been carried through.

Let us now note that for $\kappa \geqq 1/\sqrt{2}$ a peculiar instability of the normal phase of the metal occurs. Indeed, suppose the whole metal is in equilibrium, and in the normal state, i.e., $H_0 = 1/\sqrt{2}$. Then it can be shown that for $\kappa \geqq 1/\sqrt{2}$ an instability appears with respect to the formation of thin layers of superconducting phase in the sense that solutions of (18) appear with $\Psi \neq 0$. In fact, assuming that $\Psi \ll 1$, we can take $H = H_0$ = const and the first equation (18) assumes the form

$$\frac{d^2\Psi}{dz^2} = -\kappa^2(1 - H_0^2Z^2)\Psi. \tag{33}$$

This equation in its form coincides with the Schrödinger equation for the harmonic oscillator and is well known to have solutions for $\Psi$ which vanish for $z = \pm\infty$ if $\kappa = 2H_0(n + \frac{1}{2})$, where $n = 0, 1, 2, \ldots$

Since for the normal phase $H_0 \geqq 1/\sqrt{2}$, the minimum value of $\kappa$ for which solutions can appear is $1/\sqrt{2}$. The point $z = 0$ chosen in (33) is quite arbitrary, i.e., a "parasitic" solution can appear anywhere, and indeed there occurs a certain instability of the normal phase connected with the fact that when $\kappa > 1/\sqrt{2}$ the surface energy $\sigma_{ns} < 0$ (see end of section 3).

It has not been necessary to investigate the nature of the state which occurs when $\kappa > \kappa_0$ since from the experimental data, it is true somewhat preliminary and worked out on the basis of equation (22), it follows that $\kappa \ll 1$. Leaving on one side the question of the true value of $\kappa$, we must in any case, because of the indicated instability of the solution, note that all results obtained by us are valid only for the case

$$H < H_0\left(= \frac{1}{\sqrt{2}}\right).$$

We may use the solution (31) to investigate the dependence on field strength of the penetration depth of a magnetic field in a bulk superconductor[9,10]. In agreement with the experimental method of measurement[11,12] we define the penetration depth of a magnetic field in a bulk superconductor in the following way:

$$\delta = \frac{1}{H_0}\int_0^\infty H dz = \frac{\delta_0}{H_0}\int_0^\infty H dz = \delta_0 \frac{|A_0|}{H_0}, \qquad (35)$$

where $H_0$ is the external field (field at $z = 0$) and in the first expression we used the usual and in the second and third the reduced units for $H$, $H_0$, $A_0$ and $z$. Substituting the field (31) into (35) we have (in the usual units)

$$\delta = \delta_0\left\{1 + \frac{\kappa(\kappa + 2\sqrt{2})}{8(\kappa + \sqrt{2})^2}\left(\frac{H_0}{H_{cb}}\right)^2\right\} \equiv \delta_0\left\{1 + f(\kappa)\left(\frac{H_0}{H_{cb}}\right)^2\right\},$$

$$\frac{d\delta}{dT} = \frac{d\delta_0}{dT} + f(\kappa)\left(\frac{H_0}{H_{cb}}\right)^2\left\{\frac{d\delta_0}{dT} - \frac{2(dH_{cb}/dT)}{H_{cb}}\delta_0\right\}. \qquad (36)$$

From this it is clear that the quantity $\delta_0$, as already mentioned, represents the penetration depth in a weak field. The function $f(\kappa)$ grows monotonically with $\kappa$ in such a way that $f(0) = 0, f(\infty) = 1/8$, and for $\kappa \ll 1, f(\kappa) \sim \kappa/4\sqrt{2}$. Thus for $H_0 = H_{cb}$, even for $\kappa = 1/\sqrt{2}$, $\delta = 1{\cdot}07\ \delta_0$, and for $\kappa = 0{\cdot}165$, $\delta = 1{\cdot}028\ \delta_0$. If, as was the case in (12), measurements of $\delta$ are carried out using a weak and slowly varying field $H_1$ in the presence of a strong field $H_0$, then $(\delta - \delta_0)/\delta_0 = 3f(\kappa)(H_0/H_{cb})^2$, i.e., the effect is tripled. We see that the expected change of $\delta$ with $H$ for mercury, for which according to our estimate $\kappa = 0{\cdot}165$, is very small and lies outside the limits of accuracy of measurements achieved in (12) (the data of ref. 11 on the dependence of $\delta$ on $H$ are probably for reasons indicated in ref. 12 not true); this is also evident from the fact that in ref. 11 for a number of cases $\delta$ varies as $H_0$ rather than as $H_0^2$† since it is an even function of $H_0$. As we shall see in section 4 for thin superconductors the dependence of $\delta$ on $H_0$ is much bigger than for bulk ones and may be observed in experiments of the type

† Even in weak fields, where it must necessarily vary as $H_0^2$.



described in ref. 10 (thus it is possible that the dependence of $\delta$ on $H$ in ref. 10 is real, which does not contradict the absence of a noticeable effect in ref. 12).

## 3. The Surface Energy at the Boundary of the Superconducting and Normal Phases

For the calculation of $\sigma_{ns}$ we must find the solution of the equations (18) for a superconducting half-space limited by a half-space consisting of the normal phase of the same metal. Since the only difference between two phases is that in the one $\Psi \neq 0$ and in the other $\Psi = 0$, it is reasonable to suppose that the transition between the two phases takes place continuously in some transition layer. It can be shown that our equations have just such a continuous smooth solution, and do not for instance lead to a solution satisfying the conditions of the problem in which the function $\Psi$ vanishes suddenly at some point. Thus the transition from the superconducting phase to the normal takes place in a transition layer in which for $z = \infty$ we have the superconducting phase and for $z = -\infty$ the normal phase. This means that we must seek a solution of the equations (18) with the boundary conditions

$$\Psi = \Psi_\infty = 1,\ H = A = \frac{d\Psi}{dz} = 0 \text{ when } z = \infty;$$

$$\Psi = \frac{d\Psi}{dz} = 0,\ H = H_0 = \frac{1}{\sqrt{2}},\ A = H_0 z + \text{const when } z = -\infty. \qquad (37)$$

In fact, of course, the transition layer has a breadth of the order of $\delta_0$ (more precisely, as we shall see below, of the order of $\delta_0/\kappa$) just as the magnetic field in a superconductor falls to zero in a distance of the order of $\delta_0$ although strictly speaking it vanishes only at $z = \infty$.

Substituting (28) into (19) we obtain an expression for the surface energy $\sigma_{ns}$:

$$\sigma_{ns} = \frac{H_{cb}^2}{2\pi}\delta_0\int_{-\infty}^{\infty}\left\{\tfrac{1}{2} - (1 - A^2)\Psi^2 + \tfrac{1}{2}\Psi^2 - H_0 H\right\} dz$$

$$= \frac{H_{cb}^2}{2\pi}\,\delta_0 \int_{-\infty}^{\infty} \left\{ \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 + H^2 - H_0 H \right\} dz, \tag{38}$$

where the relation (28) has been used, $H_0$ has been put equal to $1/\sqrt{2}$ and all quantities under the integral sign are expressed in reduced units.

In view of the fact that the general case involves the solution of equations (18) we can give an analytical expression for $\sigma_{ns}$ only for sufficiently small $\kappa$. In this case in the superconducting phase for large $z$ (far from the transition region) $\Psi = 1 - \text{const}\, e^{-\sqrt{2}\kappa z}$ (see (30), (31)), i.e., changes only slowly with $z$. Consequently we shall seek a solution of the second equation (18) in the form

$$A = \exp\{-\int \Psi dz\}. \tag{39}$$

It is easy to see that this solution is valid, if

$$\left| \frac{d}{dz}\left(\frac{1}{\Psi}\right) \right| \ll 1. \tag{40}$$

Substituting (39) in (28) we find that $d\Psi/dz = \kappa(1 - \Psi^2)/\sqrt{2}$; i.e.,

$$\Psi = \tanh\left(\frac{\kappa z}{\sqrt{2}}\right), \tag{41}$$

provided that the origin of $z$ is suitably chosen. It should be noted that the solution (41) is at the same time the strict solution of equation (18) for $\Psi(z)$ in the absence of an external field and subject to the condition that $\Psi(\infty) = 1$ and $\Psi(0) = 0$. From (40) it is evident that the solution (41) in the presence of a field applies as long as the inequality

$$\kappa \ll \sqrt{2}\sinh^2\left(\frac{\kappa z}{\sqrt{2}}\right) \tag{42}$$

is satisfied. With this condition, and taking into account (39) and (41), we find that

$$A = \exp\{-\int \Psi dz\} = C \exp\left[-\frac{\sqrt{2}}{\kappa}\ln\cosh\left(\frac{\kappa z}{\sqrt{2}}\right)\right], \tag{43}$$



and

$$H = \frac{dA}{dz} = -\Psi A = -A\tanh\left(\frac{\kappa z}{\sqrt{2}}\right).$$

For $\kappa z \ll 1$,

$$\Psi = \frac{\kappa z}{\sqrt{2}},\quad A = C\exp\left[-\frac{\kappa z^2}{2\sqrt{2}}\right],\quad \kappa z^2 \gg 1, \tag{44}$$

where the inequality $\kappa z^2 \gg 1$ is obtained from (42). It is evident that the approximation (44) is valid if $1/\kappa \gg z \gg 1/\sqrt{\kappa}$; these inequalities may be satisfied if $\kappa$ is sufficiently small. For an estimate of the constant $C$ in (43) and (44) we take account of the fact that $H \leqq H_0 (= 1/\sqrt{2})$, and consequently $|A| \leqq 1/\sqrt{2}\tanh(\kappa z/\sqrt{2})$, or, if $\kappa z \ll 1$, $|A| \leqq 1/\kappa z$ in the region where $H \sim 1/\sqrt{2}$. From this, taking into account that equation (44) still applies as regards order of magnitude for $z \sim \kappa^{-1/2}$, we find that $C \sim \kappa^{-1/2}$. Thus at the boundary of the region of validity of the solutions (41) to (43) $A \gg 1$ (since $\kappa \ll 1$). But if $A \gg 1$ the equations (18) simplify and assume the form

$$\frac{d^2\Psi}{dz^2} = \kappa^2 A^2 \Psi;\quad \frac{d^2 A}{dz^2} = \Psi^2 A. \tag{45}$$

Introducing the variables $\zeta = z\sqrt{\kappa}, \phi = \Psi/\sqrt{\kappa}$, and $B = A\sqrt{\kappa}$, we obtain from (45) the universal equations

$$\frac{d^2\phi}{d\zeta^2} = \phi B^2;\quad \frac{d^2 B}{d\zeta^2} = \phi^2 B, \tag{46}$$

which likewise cannot be integrated analytically but must be solved numerically once and for all. However, there is no need even to do this since it is easy to see that the contribution to $\sigma_{ns}$ from the region where equations (45) and (46) are valid, i.e., the region $-\infty < z \lesssim \kappa^{-1/2}$ is of the order $\kappa^{-1/3}$. Similarly the contribution from the region $\kappa^{-1/2} < z < \infty$ is of the order of $\kappa^{-1}$. Indeed, substituting into (38) the solutions (41) and (43) it is easy to see that the contribution to $\sigma_{ns}$ from the terms $H^2 - H_0 H$ under the integral sign is a quantity of order $\kappa^{-1/2}$ while

$$\int_{1/\sqrt{\kappa}}^{\infty} \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 dz = \frac{\sqrt{2}}{3\kappa} + \text{terms of the order } \kappa^{-1/2};$$

the higher order terms are connected with the lower limit of the integral. In this way, apart from terms of the order of $\kappa^{-1/2}$, we have

$$\sigma_{ns} = \frac{\delta_0 H_{cb}^2}{3\sqrt{2\pi\kappa}}, \quad \Delta = \frac{\sigma_{ns}}{H_{cb}^2/8\pi} = \frac{1{\cdot}89\delta_0}{\kappa}, \text{ if } \sqrt{\kappa} \ll 1. \tag{47}$$

It is especially important to emphasise that, for small values of $\kappa$, $\sigma_{ns} > 0$, which is absolutely necessary, and the attainment of which was our main aim. For sufficiently large $\kappa$, on the other hand, $\sigma_{ns} < 0$ (this is apparent immediately from (38) since $H^2 < H_0 H$), which indicates that such large values of $\kappa$ do not correspond to the usually observed state of affairs (as a result of a numerical integration it turns out that $\sigma_{ns} = 0$ when $\kappa = 1/\sqrt{2}$). The value (23) assumed by us for mercury is very small from all other points of view but insufficiently small for the applicability of (47), since in this case $\sqrt{\kappa} = 0{\cdot}407$. The numerical integration for $\kappa = 0{\cdot}165$ leads to a value of about $6\delta_0$ for $\Delta$, while according to (47) $\Delta = 11{\cdot}4\delta_0$.

The thickness of the transition layer is evidently of the order of $\delta_0/\kappa$, i.e., about $10\delta_0$.

## 4. Superconducting Plates (Films)

The solution is one dimensional for plane plates and films as well as for a half space. Here it is of interest to calculate the critical magnetic field, $H_c$, for destruction of superconductivity in films and the magnetic moment of the film in an arbitrary field $H_0$; moreover when there is a total current $J$ flowing through the film we have to find the critical value of the current $J_c$ to destroy superconductivity, and also the dependence of $J_c$ on a superimposed field $H_0$.

The critical field $H_c$, as is shown by thermodynamic considerations [2,3], is determined by the relations

$$\frac{H_c^2}{8\pi} = \frac{H_{cb}^2}{8\pi} - \frac{\sigma}{d},$$

$$\sigma = \int_0^d \left( \frac{H^2(z)}{8\pi} - \frac{H_c H(z)}{4\pi} + \Delta F \right) dz, \tag{48}$$



in which the thickness of the plate is $2d$, the $z$-axis is perpendicular to the plate with $z = 0$ at its centre, $H_{cb}$ is the critical field for a bulk superconductor and $\Delta F$ is the contribution to the free energy density of the superconductor resulting from penetration of the magnetic field. In the theory based on equation (1), $\Delta F = \Lambda j_s^2/2$, and substitution of equation (4) into (48) leads to equation (5), if surface energy is ignored. In our case we obtain from (9) and (7)

$$\Delta F = F_{no} + \alpha\Psi^2 + \tfrac{1}{2}\beta\Psi^2 + \frac{\hbar^2}{2m}\left(\frac{d\Psi}{dz}\right)^2 + \frac{e^2}{2mc^2}A^2\Psi^2 - \left(F_{no} - \frac{\alpha^2}{2\beta}\right),$$

and thus

$$\sigma = \frac{H_{cb}^2\delta_0}{4\pi}\int_0^d \left\{ \tfrac{1}{2} - (1 - A^2)\Psi^2 + \tfrac{1}{2}\Psi^4 + \frac{1}{\kappa^2}\left(\frac{d\Psi}{dz}\right)^2 + H^2 - 2H_c H \right\} dz, \tag{48a}$$

in which the new units are used in the integrand. The quantity (48a) is denoted by $\sigma$ since it is clear from (15) that it is equivalent to the surface energy integrated with the proper limits.

The magnetic moment of the film per unit area in an external field $H_0$, parallel to the film, is given by

$$\mu = \int_{-d}^{d} \frac{H(z) - H_0}{4\pi}\, dz = \frac{1}{2\pi}(A(d) - H_0(d)), \tag{49}$$

where in the transition to the second expression it has been taken into account that for a film without a total current in an external field $H(z) = H(-z)$. $A(d)$ has been substituted for

$$\int_0^d H(z)dz,$$

since the potential $A$ will be chosen below in such a way that $A(0) = 0$. Equation (49) can be obtained either from the fact that the work of magnetisation of the film is given by

$$-\mu H_0 = \frac{H_0}{4\pi}\int (H_0 - H(z))dz$$

or directly, from the fact that the field $H(z)$ plays the role of magnetic induction $B(z)$, and thus the expression $(H(z) - H_0)/4\pi$ is equivalent to the magnetisation $M = (B - H)/4\pi$.

For the determination of $H_c$, $\mu$ and $J_c$ we must find the solution of equations (18) with the boundary conditions

$$\frac{d\Psi}{dz} = 0,\ H = H_0 \pm H_J,\ H_J = \frac{2\pi}{c} J, \text{ when } z = \pm d. \tag{50}$$

Here $H_0$ is the external magnetic field directed along the $y$-axis $J$, is the total current

$$\left(J = \int_0^d j dz, \text{ where } j \text{ is the current density}\right)$$

flowing along the film in the direction of the negative $x$-axis, and $2H_J(= 4\pi J/c)$ is the difference between the values of the total field on both sides of the film due to the current $J$. If the current $J$ and the field $H_0$ are not mutually perpendicular then there are two non-vanishing components of the potential $A$ (in fact $A_x$ and $A_y$) instead of the single component $A_x$ in the case considered above. We should then have instead of (18) a system of initial equations of the form

$$\frac{d^2\Psi}{dz^2} = \kappa^2\{-(1 - A_x^2 - A_y^2)\Psi + \Psi^3\},$$

$$\frac{d^2A_x}{dz^2} = \Psi^2 A_x,\ \frac{d^2A_y}{dz^2} = \Psi^2 A_y. \tag{51}$$

These equations have to be solved for the conditions

$$H_x = H_{x0},\ H_y = H_{y0} \pm H_J,$$

$$H_J = \frac{2\pi J}{c},\ \frac{d\Psi}{dz} = 0, \text{ when } z = \pm d. \tag{52}$$

The axes have now been chosen in such a way that the total current has a component only along the $x$-axis and consequently the field $H_J$ is directed along the $y$-axis; $H_{x0}$ and $H_{y0}$ are the components of the external field along the $x$- and $y$-axes.

For sufficiently thick plates, i.e., when $d \gg \delta_0$, the value $H_c$ may be immediately obtained from the results of section 2 by



allowing $d$ to tend to infinity in (48). Thus substituting the solution (31) into (48) we have, for $d \gg \delta_0$,

$$\frac{H_c}{H_{cb}} = 1 + \frac{\delta_0}{2d}\left(1 + \tfrac{1}{2}f(\kappa)\right). \tag{53}$$

Here $f(\kappa) = \kappa(\kappa + 2\sqrt{2})/8(\kappa + \sqrt{2})^2$, the same function as in (36); equation (53) is valid up to terms of the order $(\delta_0/d)^2$. To the same approximation in the usual theory[1,2] we should obtain the expression (53) with $\kappa = 0$ (see (5)). Taking (36) into account, equation (53) may be written in the form

$$\frac{H_c}{H_{cb}} = 1 + \frac{\delta_0}{2d} + \frac{\Delta\delta}{4d}, \tag{54}$$

where $\Delta\delta = \delta(H_{cb}) - \delta_0$.

For films of arbitrary thickness the solution of (18) must be carried out again. The solution of (31) suggests that for thin plates as well as for thick ones the function $\Psi$ changes only slowly with $z$, if $\kappa$ is small. Starting from this supposition, which is subsequently justified, we suppose that

$$\Psi = \Psi_0 + \phi,\ |\phi| \ll \Psi_0, \text{ and } \phi = 0 \text{ when } z = 0. \tag{55}$$

Then equations (18) in the first approximation assume the form

$$\left.\begin{aligned} \frac{d^2\phi}{dz^2} &= \kappa^2\{\Psi_0^3 - \Psi_0 + (3\Psi_0^2 - 1)\phi + A^2\Psi_0\}, \\ \frac{d^2A}{dz^2} &= \Psi_0^2 A. \end{aligned}\right\} \tag{56}$$

From the second of the equations (56), taking account of the boundary conditions (50), we find the values of $A$ and $H$ to be

$$\left.\begin{aligned} A &= \frac{H_0 \sinh \Psi_0 z}{\Psi_0 \cosh \Psi_0 d} + \frac{H_J \cosh \Psi_0 z}{\Psi_0 \sinh \Psi_0 d}, \\ H &= \frac{dA}{dz} = \frac{H_0 \cosh \Psi_0 z}{\cosh \Psi_0 d} + \frac{H_J \sin \Psi_0 z}{\sinh \Psi_0 d}. \end{aligned}\right\} \tag{57}$$

Substituting (57) in the first of the equations (56) we find $\phi$, and from the requirement that for $z = \pm d$, $d\phi/dz = 0$, we obtain a transcendental equation determining $\Psi_0$.

As we shall see in practice we may with sufficient accuracy put $\kappa = 0$. We shall therefore give the expression for $\phi$ and the equations for $\Psi_0$ for the case $\kappa \neq 0$ only when $H_J = 0$, i.e., for a film in an external field. In this special case

$$\phi = -\frac{\Psi_0(\Psi_0^2-1)}{3\Psi_0^2-1}\{1-\cosh \kappa z\sqrt{3\Psi_0^2-1}\}$$

$$+\frac{\kappa H_0^2}{2\Psi_0^2\sqrt{3\Psi_0^2-1}\cosh^2\Psi_0 d}\left\{\frac{1-\cosh\kappa z\sqrt{3\Psi_0^2-1}}{\kappa\sqrt{3\Psi_0^2-1}}\right.$$

$$\left.\frac{\kappa\sqrt{3\Psi_0^2-1}\,(\cosh\kappa\sqrt{3\Psi_0^2-1}\,z-\cosh 2\Psi_0 z)}{4\Psi_0^2-\kappa^2(3\Psi_0^2-1)}\right\}, \tag{58}$$

$$\Psi_0^2-1=\frac{2H_0^2\left\{1-\dfrac{\sinh 2\Psi_0 d}{2\Psi_0 d}\,\dfrac{\kappa d\sqrt{3\Psi_0^2-1}}{\sinh \kappa d\sqrt{3\Psi_0^2-1}}\right\}}{\cosh^2\Psi_0 d\{4\Psi_0^2-\kappa^2(3\Psi_0^2-1)\}} \tag{59}$$

In the limiting case $\kappa = 0$, for arbitrary $H_0$ and $H_J$, naturally $\phi = 0$ and

$$\Psi_0^2(\Psi_0^2-1)=\frac{H_0^2\left(1-\dfrac{\sinh 2\Psi_0 d}{2\Psi_0 d}\right)}{2\cosh^2\Psi_0 d}-\frac{H_J^2\left(1+\dfrac{\sinh 2\Psi_0 d}{2\Psi_0 d}\right)}{2\sinh^2\Psi_0 d}. \tag{60}$$

Let us note that for $\kappa = 0$ the equation for $\Psi(= \Psi_0 = \text{const})$ may be immediately obtained from the condition of minimum free energy, i.e., from the condition $d\sigma/d\Psi = 0$. It is clear from (48), that this condition gives

$$\Psi_0^2-1=\frac{1}{d}\int_0^d A^2 dz,$$

which leads to (60).

Let us now discuss in somewhat more detail the destruction of superconductivity in a film by an external field in the absence of a total current. If $\kappa = 0$, then $\Psi = \Psi_0 = \text{const}$ and the solution (57) applies with $H_J = 0$. Substituting this solution in (48) we easily find (in the usual units)



$$\left(\frac{H_c}{H_{cb}}\right)^2=\frac{\Psi_0^2(2-\Psi_0^2)}{1-\dfrac{1}{\eta}\tanh\eta},\ \text{where } \eta=\frac{\Psi_0 d}{\delta_0}. \tag{61}$$

In this case ($\kappa = 0$, $H_J = 0$) equation (60) becomes, when $H_0 = H_c$ or in the usual units when $H_0 = H_c/\sqrt{2}H_{cb}$,

$$\left(\frac{H_c}{H_{cb}}\right)^2=\frac{4\Psi_0^2(\Psi_0^2-1)\cosh^2\eta}{1-(\sinh 2\eta)/2\eta},\ \text{where } \eta=\frac{\Psi_0 d}{\delta_0}. \tag{62}$$

From (61) and (62), from the measured values of $H_c/H_{cb}$ and from $d$,we can determine $\Psi_0$ and $\delta_0$. It is easy to see that for small values of $\eta$ and for $H = H_c$, $\Psi_0 = 0$ and

$$\frac{H_c}{H_{cb}}=\sqrt{6}\,\frac{\delta_0}{d}. \tag{63}$$

Thus in this case we have a second order phase change; with increasing field, $\Psi_0$ decreases and at the transition point $\Psi_0 = 0$. As is evident from (60), for $H_J = 0$, up to terms of order $d^2$ (taking into account that $H_0^2 d^2$ may be of the order unity) we have

$$\Psi_0^2=\frac{1-(H_0/H_{cb})^2(d^2/6\delta_0^2)}{1-\frac{2}{15}(H_0/H_{cb})^2(d^4/\delta_0^4)}.$$

The transition to the normal state is a second order one for $d \leqq d_c$, where it is easily shown from (61) and (62) that

$$d_c=\sqrt{5}\delta_0/2. \tag{64}$$

The point $d = d_c$ is a kind of critical Curie point[7], and for $d > d_c$ we have a first order transition; i.e., for $H_0 = H_c$, $\Psi_0 > 0$ and there is a latent heat of transition (for $d < d_c$ and for $H_0 = H_c$ we have a jump in the specific heat; the specific heat of thin plates evidently depends on $H_0$).

The penetration depth of the field is clearly from (57) the quantity

$$\delta=\frac{\delta_0}{\Psi_0}, \tag{65}$$

and we see that for sufficiently thin specimens the penetration depth may be appreciably larger than for the bulk metal when $H_0 \sim H_c$.

Here (see (49) and (57) with $H_J = 0$)

$$\mu = -\frac{H_0 d}{2\pi}\left(1 - \frac{\delta}{d}\tanh\frac{d}{\delta}\right) = -\left(\frac{H_0 d}{2\pi}\right)\left\{\frac{1}{3}\left(\frac{d}{\delta}\right)^2 - \frac{2}{15}\left(\frac{d}{\delta}\right)^4 + \dots\right\}. \tag{66}$$

From measurements of $\mu$ we may find the penetration depth $\delta$ which according to (65) and (60) depends on $H_0$.

For $\kappa \neq 0$ all the expressions become exceedingly complicated in the general case. However, for small values of $\kappa$, which are the only ones which interest us, and for not too large values of $d$, we may expand all the expressions as series in $\kappa d$. The result is that, in the range of thicknesses for which the transition is a second order one, equation (63) must be replaced by the expression:

$$\left(\frac{H_c}{H_{cb}}\right)^2 = 6\left(\frac{\delta_0}{d}\right)^2 - \frac{7}{10}\kappa^2 + \frac{11}{1400}\kappa^4\left(\frac{d}{\delta_0}\right)^2 \dots \tag{67}$$

The value of $d_c$ is then given by

$$d_c^2 = \frac{5}{4}\left(1 - \frac{7}{24}\kappa^2 + \dots\right)\delta_0^2. \tag{68}$$

If we take for $\kappa^2$ the value (23) then in practice it is hardly necessary to take into account the term in $\kappa^2$ in (67), (68) and in the analogous expressions.

The only experimental data on destruction of superconductivity in films by an external field suitable for a quantitative discussion are those given in ref. 4 and refer to mercury. The scatter of points, however, even in these measurements was rather large, and moreover in the absence of tables the values of $H_c/H_{cb}$ had to be taken from graphs; nevertheless the chief source of error is due to the fact that the thickness of the films indicated in ref. 4 is some sort of average value and may, especially for the thin films, differ considerably from the thickness $d$ entering in our formulae in which it is assumed of course that the film is ideally uniform.

In Table 1 we reproduce the values of $\delta_0$ obtained with the aid of (63) on the basis of the data for $H_c/H_{cb}$ as a function of $d$ given in ref. 4; the values shown in brackets are those for which the calculation from equation (63) is already invalid since $d > d_c$. Underneath



these values in brackets are put the values of $\delta_0$ obtained directly from equations (61) and (62).

In the last column are shown the values of $2d_c$ obtained from equation (64) with the help of the minimum values of $\delta_0$ in the corresponding line. From Table 1, as also directly from the graph given in ref. 4 showing the dependence of ln $(H_c/H_{cb})$ on ln $2d$, it is

TABLE 1. Values of $\delta_0$ for mercury ($\delta_0$ and $d$ in units of $10^{-5}$ cm)

| $2d$ / $T$°K | 0·596 | 0·840 | 1·178 | 1·423 | 1·690 | 2·400 | 4·390 | 10·880 | $2d_c = \sqrt{5}\delta_{0\min}$ |
|---|---|---|---|---|---|---|---|---|---|
| 4·13 | 5·13 | 4·61 | 4·07 | 4·17 | 3·80 | 3·37 | 3·08 | (3·72)<br>3·56 | 6·9 |
| 4·12 | 4·12 | 4·06 | 3·47 | 3·36 | 3·27 | 3·11 | 2·72 | (3·52)<br>3·30 | 6·1 |
| 4·10 | 3·47 | 3·38 | 2·87 | 3·02 | 2·79 | 2·53 | 2·28 | (3·21)<br>2·50 | 5·1 |
| 4·05 | 2·66 | 2·62 | 2·32 | 2·27 | 2·08 | 1·86 | (1·80)<br>1·80 | (2·86)<br>1·95 | 4·0 |
| 4·00 | 2·28 | 2·31 | 1·92 | 1·82 | 1·76 | 1·56 | (1·57)<br>1·57 | (2·72)<br>1·70 | 3·5 |
| 3·80 | 1·69 | 1·62 | 1·40 | 1·28 | 1·24 | 1·10 | (1·31)<br>1·15 | (2·63)<br>1·39 | 2·5 |
| 3·60 | 1·27 | 1·24 | 1·08 | 0·99 | 0·98 | (0·87)<br>0·87 | (1·23)<br>0·99 | (2·50)<br>1·16 | 1·95 |
| 3·00 | 1·10 | 1·10 | 0·92 | 0·84 | (0·83)<br>0·83 | (0·77)<br>0·72 | (1·16)<br>0·84 | — | 1·61 |
| 2·50 | 0·92 | 0·94 | 0·86 | 0·80 | (0·75)<br>0·75 | (0·73)<br>0·66 | (1·13)<br>0·78 | (2·45)<br>1·0 | 1·48 |

clear that there is a sharp break in the course of this dependence which sets in as $d$ passes through $d_c$ (in Table 1 the single values of $\delta_0$ and the values in brackets according to (63) are simply quantities proportional to $(H_c/H_{cb})d$; this product falls as $d$ rises to $d_c$ and for $d > d_c$ the sharp rise begins). We are inclined to regard this behaviour as confirmation of the conclusion that the character of the transition is different for $d < d_c$ and $d > d_c$. The fall of the values of $\delta_0$ with rise of $d$, clearly evident from Table 1 for $d > d_c$, may be completely explained by the already mentioned difference between the values of $d$ indicated in ref. 4 and the effective values $d_{eff}$. Alternatively it is evident that the thinner the film the more will $d_{eff}$ depart from $d$, and that $d_{eff} < d$. The observed dependence of $\delta_0$ on $d$ for $d < d_c$ is in agreement with this picture; but we can see no reason for the increase with $d$ of the values of $\delta_0$ calculated according to (61) and (62) when $d > d_c$.

We must however bear in mind two considerations. First, the whole of our scheme based on the expansion of $F_{so}$ and (10) in powers $\Psi^2$ up to the terms in $\Psi^4$ is generally speaking valid only in the region close to $T_c$ in which the relation (8) and the equation

$$\delta_0^2 = \frac{\text{const}}{T_c - T} = \frac{\delta_{00}^2}{1 - T/T_c}, \tag{69}$$

are valid, where $\delta_{00}$ is a certain constant (see (20) and (7)). For mercury the region, where (8) is valid and therefore (69) should be applicable, lies between $T_c$ and $T \sim 3{\cdot}80$–$4{\cdot}0$°K. For smaller values of $T$ we must in general take into account higher terms in the series expansion of $F_{so}$ (i.e., terms in $\Psi^5$ etc. in (18)) and the application of all the formulae obtained without the substitution of $|\alpha|/\beta$ by $(d\alpha/dT)_c\,(T_c - T)/\beta_c$ is possible only if the non-linear dependence of $|\alpha|/\beta$ on $(T_c - T)$ is more important than the influence of terms in $\Psi^6$ etc. Such a situation is possible, but it could not be assumed to occur unless it were demonstrated by an analysis of sufficiently extensive experimental data; this is not possible at present owing to the absence of the latter. In view of what has been said, the data of Table 1 for $T < 3{\cdot}80$°K may be distorted.

The second consideration which we must bear in mind is that $T_c$ varies considerably from film to film; in ref. 4 all the data were reduced to $T_c = 4{\cdot}167$°K and this operation, evidently inaccurate for $T = 4{\cdot}12$°K and $T = 4{\cdot}13$°K, may also influence the data in Table 1 at lower temperatures. The whole question clearly requires a more detailed experimental investigation; for the moment we shall take for $\delta_0$ the lowest of the values in Table 1 and compare them with the data obtained by other methods [10,12]. In doing this we must consider the fact that in ref. 12 the quantity directly measured was only $\delta_0 - \delta_0(2{\cdot}5°)$, and that $\delta_0$ was calculated by means of an extrapolation which does not appear *a priori* valid.



The values of $\delta_0$ obtained in ref. 10 are based on the previous measurements with the colloids and are likewise inaccurate; here also the measured quantity was $\delta_0 - \delta_0(2{\cdot}5°)$. As can be seen from Table 2, in which all the quantities must be multiplied by $10^{-5}$ cm within the limits of the accuracy achieved up to the present time the data of Table 1 coincide with those obtained by other methods (we must especially emphasise that the data of ref. 12 relate to bulk specimens).

TABLE 2.

| $T$°K | $\delta_0$ from Table 1 | $\delta_0-\delta_0(2{\cdot}5)$° from Table 1 | $\delta_0$ from ref. 10 | $\delta_0-\delta_0(2{\cdot}5°)$ from ref. 10 | $\delta_0$ from ref. 12 | $\delta_0-\delta_0(2{\cdot}5°)$ from ref. 12 |
|---|---|---|---|---|---|---|
| 4·13 | 3·08 | 2·42 | 4·08 | 3·28 | 2·28 | 1·82 |
| 4·12 | 2·72 | 2·06 | 3·57 | 2·77 | 2·04 | 1·58 |
| 4·10 | 2·28 | 1·62 | 2·80 | 2·00 | 1·72 | 1·26 |
| 4·05 | 1·80 | 1·14 | 2·34 | 1·54 | 1·31 | 0·85 |
| 4·00 | 1·56 | 0·90 | 1·95 | 1·15 | 1·10 | 0·64 |
| 3·80 | 1·10 | 0·44 | 1·38 | 0·58 | 0·77 | 0·31 |
| 3·50 | 0·87 | 0·21 | — | — | 0·61 | 0·15 |
| 3·00 | 0·72 | 0·06 | — | — | 0·50 | 0·04 |
| 2·50 | 0·66 | 0·00 | 0·80 | 0·00 | 0·46 | 0·00 |

Assuming for $\delta_0$ the values indicated in the second column of Table 1 we may calculate $\kappa$ with the help of (22) taking also into account the fact that for mercury close to $T_c$, $H_{cb} = 187(T_c - T)$. Thus if we use the most reliable value of $\delta_0$ at 4°K we obtain the result (23). Using the value of $\delta_0$ indicated in ref. 12 for mercury and for tin we obtain $\kappa \sim 0{\cdot}015$.

Let us now turn to the question of the destruction of superconductivity of a film by a current. For $\kappa = 0$ the function $\Psi_0$ in the presence of a current is given by equation (60), which for $d \ll 1$ takes the form

$$\Psi_0^2 = 1 - \frac{H_0^2 d^2}{3} - \frac{H_J^2}{\Psi_0^4 d^2}. \tag{70}$$

The field $H_J$ as a function of $\Psi_0$ becomes zero for $\Psi_0 = 0$ and for some non-vanishing value of $\Psi_0$ (if $H_0 = 0$ then $H_J = 0$ for $\Psi_0 = 1$);

between these two values of $\Psi_0$, $H_J$ exhibits a maximum. In other words the function $\Psi_0$ for given $H_J$ may according to (70) have two values. It is easy to see that the superconductivity of a film is stable only so long as the field $H_J$ of the current grows with decrease of $\Psi_0$ (in this case the free energy is less than that corresponding to the same $H_J$ but a lower value of $\Psi_0$). The critical field $H_{Jc}$ is determined from the condition $dH_J/d\Psi_0 = 0$, which leads to the relation

$$\frac{H_c}{H_{cb}} = \frac{2\sqrt{2}}{3\sqrt{3}} \cdot \frac{d}{\delta_0}\left[1 - \left(\frac{H_0}{H_c^2}\right)^2\right]^{3/2}, \tag{71}$$

where $H_c$ is the critical field of a given film in the absence of a current, $H_0$ is the external field and $J_c$ is the critical current ($H_{Jc} = (2\pi/c)J_c$). In the absence of a field $H_0$ we have

$$\frac{H_{Jc}}{H_{cb}} = \frac{2\sqrt{2}}{3\sqrt{3}} \cdot \frac{d}{\delta_0}. \tag{72}$$

For the case of arbitrary relative orientations of $H_0$ and $H_J$, where we must use equations (51) with the boundary conditions (52), it is easy to see that we obtain the previous equations (60), (70) and (71) with $H_0^2 = H_{x0}^2 + H_{y0}^2$ (the current $J$ is directed along the negative $x$-axis, the field $H_J$ along the $y$-axis). It should be noted that it follows from (63) and (72) for sufficiently thin films that

$$H_c H_{Jc} = \frac{4}{3} H_{cb}^2. \tag{73}$$

Thus although the values of $H_c$ and $H_{Jc}$ for thin films may be greatly different from $H_{cb}$, the product $H_c H_{bc}$, which is equal for a massive specimen to $H_{cb}^2$ is multiplied by a factor 4/3 for the very thinnest films. Relations (71) and (72) are in qualitative agreement with experiments from which, however, it is impossible to draw quantitative conclusions.

Summarising we may indicate that for an experimental verification of the theory there is a whole number of possibilities; measurement of the critical field and current for films [(61),(62),(63), and (72)]; measurement of the influence of field on the critical current [see (71)]; measurement of the magnetic moment [see (65) and (66)]; measurement of $\sigma_{ns}$ and, finally, measurement of $\delta(H_0)$ for bulk superconductors [see (36) and (53)]. However, working with films, a direct determination of $\kappa$ (if it is really small) is in practice apparently not possible. Thus for the determination of $\kappa$ not using (23) we must either determine $\sigma_{ns}$—a quantity which is particularly sensitive to $\kappa$—or carry out exact ($\sim$ 1 per cent) measurements with bulk superconductors of the influence on $\delta$ of fields of the order of $H_{cb}$.



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