Critical-temperature enhancement in thin superconducting films due to field dependence of the coherence length

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Nucleation of superconductivity in a thin film situated in a parallel magnetic field is considered. The field dependence of the coherence length is taken into account. In particular, the known result for the nucleation field H near the critical temperature T_c is shown to hold only in the dirty limit. If a certain condition imposed upon the thickness and the effective mean free path of the film is met (the film should be clean enough and sufficiently thin), the phase boundary $H(T)$ bends to temperatures $T>T_c$. A criterion for the anomalous phase boundary to occur is obtained. The method to calculate the whole curve $H(T)$ is developed. Possible enhancement of the critical temperature, $T_c(H)-T_c(0)$, is evaluated and shown to be substantial for a proper set of film parameters.

I. INTRODUCTION

The concept of the coherence length ξ plays a major role in the description of superconductivity. This length determines the scale of spatial variations for physical quantities that characterize the superconducting phase. Its importance notwithstanding, ξ is not among the basic microscopic input parameters of the Bardeen-Cooper-Schrieffer (BCS) (or Gorkov) theory such as Fermi velocity v, the density of states, the electron-phonon interaction strength, or the mean free path l. Rather, the coherence length might be considered as one of the quantities to be calculated with the help of the microscopic theory. Moreover, for arbitrary magnetic field H and temperature T, it is not easy to define exactly what one means while assigning a certain value to the parameter ξ. The difficulty comes, of course, from the nonlinearity of equations governing superconductivity. There exists, however, one particular region, namely, near the second-order phase transition, where the theory can be linearized and consequently the coherence length is well defined.

For an arbitrary concentration of nonmagnetic impurities, the linearization was performed by Helfand and Werthamer in their work on the upper critical field $H_{c2}(T)$ of bulk superconductors.[1] They have shown that at the curve $H_{c2}(T)$, the pair potential Δ satisfies, for any T and l, a linear homogeneous equation

$$-\xi^2(T,l)\Pi^2\Delta(\mathbf{r})=\Delta(\mathbf{r})\ . \tag{1}$$

Here the gauge invariant gradient $\mathbf{\Pi}=\nabla+2\pi i\,\mathbf{A}/\phi_0$, $\mathbf{A}$ is the vector potential, and ϕ_0 is the flux quantum. The very structure of this equation shows that the scale at which Δ changes in space, is determined by ξ.

Equation (1) is analogous to the Schrödinger equation for a particle in a uniform magnetic field. Its lowest eigenvalue corresponds to the highest field, H_{c2}, at which superconductivity first nucleates in a bulk sample:

$$H_{c2}=\phi_0/2\pi\xi^2\ . \tag{2}$$

Then, the quantity $\xi(T,l)$ [or $H_{c2}(T,l)$] is obtained by inserting (2) into the basic self-consistency equation of the theory which relates the pair potential to the anomalous Gorkov Green's function. The result reads as

$$\frac{\hbar}{2\pi T}\ln\frac{T_c}{T}=\sum_{\omega(>0)}\left[\frac{1}{\omega}-\frac{2\tau S}{\beta-S}\right], \tag{3}$$

where

$$S(H_{c2})=\frac{2\beta}{lq}\int_0^\infty e^{-u^2}\tan^{-1}\frac{ulq}{\beta}du =\sum_{j=0}^{\infty}(-1)^j\frac{j!}{2j+1}\left[\frac{lq}{\beta}\right]^{2j}, \tag{4}$$

$$\beta=1+2\omega\tau,\quad q^2=2\pi H_{c2}/\phi_0\ . \tag{5}$$

Here $\omega=\pi T(2n+1)/\hbar$ is the Matsubara frequency and $\tau=l/v$ is the relaxation time for nonmagnetic scatterers. The power series representation of S in Eq. (4) is obtained by expanding $\tan^{-1}$ and then by integrating over u.

Thus, strictly speaking, the coherence length $\xi(T,l)$ is defined *at the phase boundary* by solving Eq. (3) for $H_{c2}(T,l)$ and then by using Eq. (2), which is generally accepted as the definition of the coherence length. Still, one wonders whether or not this same definition of ξ is useful out of the immediate vicinity of the curve $H_{c2}(T)$. In fact, in a variety of systems (finite samples, proximity systems) the second-order phase transition may occur far from the bulk $H_{c2}(T)$ curve. Therefore, to approach the problem of the phase boundary in these systems, one should be able to evaluate $\xi(H,T)$ in a wide domain of the H-T plane away from $H_{c2}(T)$. A method for this evaluation has been proposed by one of the authors in Ref. 2. We summarize briefly the relevant results of this work.

Near the second-order transition from the normal to the superconducting phase (for whatever system and wherever it occurs) equations of superconductivity can be linearized. Using the Eilenberger quasiclassical version of the Gorkov's theory, one can show that the Eilenberger Green's functions averaged over the Fermi surface, $F(\mathbf{r},\omega)$, satisfy an equation similar to Eq. (1),

$$\Pi^2 F = k^2 F \ , \tag{6}$$

if the quantity k^2 is chosen as to satisfy the self-consistency equation (3). In general, however, $S(H_{c2})$ of Eq. (4) should be replaced by the following $S(H,T,k,\omega)$:[3]

$$S=\sum_{m,j=0}^{\infty}\frac{(-q^2)^j}{j!(2m+2j+1)}\left[\frac{(m+j)!}{m!}\right]^2\left[\frac{l}{\beta}\right]^{2m+2j}\times\prod_{i=1}^{m}[k^2+(2i-1)q^2]\ ,$$
$$q^2=2\pi H/\phi_0\ . \tag{7}$$

To find the phase boundary $H(T)$ at which superconductivity nucleates in a particular system, one should first consider the eigenvalue problem for Eq. (6) [recall that the lowest eigenvalue corresponds to the maximum field at which Eq. (6) has a nontrivial solution]. The eigenvalue, of course, depends on boundary conditions imposed upon solutions F. For instance, in a bulk sample, F must be finite everywhere thus making the eigenvalue problem identical to that of the harmonic oscillator. One obtains then in the present notation $H=-\phi_0 k^2/2\pi$ or $k^2=-q^2$. In the cumbersome series (7) only the term $m=0$ survives and the sum S coincides with that given in Eq. (4).

In finite samples or in proximity systems, boundaries or interfaces result in different boundary conditions. In turn, the minimum eigenvalue differs from $k^2=-q^2$, and the evaluation of the sum S becomes more involved. An exception is the case of zero field in which the sum (7) converges to

$$S=\sum_{m=0}^{\infty}\frac{(kl/\beta)^{2m}}{2m+1}=\frac{\beta}{kl}\tanh^{-1}\left[\frac{kl}{\beta}\right]\ , \tag{8}$$

if $|kl/\beta|<1$. This allows one to consider the problem of the zero-field critical temperature in proximity systems out of the dirty limit (for more detail see Ref. 2).

For an approximate evaluation of S in materials with a short mean free path, one observes that S is a series in powers of l. Keeping in (7) only terms with $m+j=0,1$, one obtains

$$S=1+\frac{l^2k^2}{3\beta^2},\quad l^4k^4\ll 1,\quad l^4q^4\ll 1\ . \tag{9}$$

When substituted in Eq. (3), this yields the de Gennes—Maki dirty limit equation for $k^2(T,l)$ (or for $H_{c2}=-\phi_0 k^2/2\pi$).[1,4] It is worth noting that in this limit the quantity S is field independent (all terms containing q are neglected). As a result, the coherence length $\xi=|k^{-1}|$ is also field independent. Thus, in the dirty limit the coherence length determined at the upper critical field at a given T, is the same at this T for any H. In other words, $\xi^2(T)=\phi_0/2\pi H_{c2}(T)$ can be used to describe the second-order phase transition at whatever field it occurs.

However, already the first correction to the dirty limit [retain in the series (7) terms up to $m+j=2$] introduces the H dependence of S:

$$S=1+\frac{l^2k^2}{3\beta^2}+\frac{l^4}{5\beta^4}(k^4+q^4),\quad l^6k^6\ll 1,\quad l^6k^2q^4\ll 1\ . \tag{10}$$

Consequently, k is also field dependent. [In estimating the neglected terms in (10) we took into account that S cannot depend upon odd powers of H, so that there are no terms in (7) proportional to q^2 or q^6.] The phase boundary $H(T)$ of a system under consideration, evaluated with the field dependent ξ defined as $|k^{-1}(H,T)|$, will certainly differ from that calculated with $\xi=|k^{-1}(H_{c2},T)|$ given in Eq. (2). To the best of our knowledge, the first attempt to include the H dependence of ξ in the evaluation of the phase boundary in a superconducting-normal multilayer, has been made in Ref. 5. It was shown that even for short l in the normal component of the multilayer, replacement of the traditional H independent ξ with $\xi(H,T)$ results in a substantial enhancement in the calculated perpendicular upper critical field. Perhaps, the most surprising changes due to the H dependence of ξ are expected to occur in thin and clean films.[6]

In Sec. II we give a short account of Ref. 6, where the discussion is restricted to a narrow region near T_c and $H=0$. In Sec. III we derive an integral representation for S which is more amenable to the numerical evaluation in a wide domain of H's and T's than the asymptotic series (7). Numerical results for the phase boundary of a thin film are given in Sec. IV. A short discussion concludes the paper.

II. PHASE BOUNDARY OF THIN FILM FOR $T \to T_c$ AND $H \to 0$

The truncation we resort to in writing Eqs. (9) and (10) for dirty and moderately dirty situations, can be used whenever the dimensionless parameters lk and lq are small. This is clearly the case if one is interested in the phase boundary $H(T)$ for $T\to T_c$ and $H\to 0$. In this limit both k and q tend to zero and, therefore, Eq. (10) holds for any l. It is shown in Ref. 6 (see also Ref. 7) that substitution of Eq. (10) in the self-consistency equation (3) results in the following field dependence of k^2:

$$k^2(H,T)=k^2(0,T)-3l^2q^4\gamma(\lambda)/5\ ,$$
$$\gamma(\lambda)=\lambda^2 N/D\ ,$$
$$N=\sum_{n=0}^{\infty}(2n+1)^{-2}(2n+1+\lambda)^{-3}\ ,$$
$$D=\sum_{n=0}^{\infty}(2n+1)^{-2}(2n+1+\lambda)^{-1}\ , \tag{11}$$

with the impurity parameter $\lambda=\hbar v/2\pi T_c l$ and with $k(0,T)$ related to the well-known Ginzburg-Landau (GL) coherence length:

$$-k^{-2}(0,T)=\xi_{\rm GL}^2=\frac{\pi T_c^2 l^2}{3\hbar\tau(T_c-T)}\sum_{\omega(>0)}\omega^{-2}\beta^{-1}\ . \tag{12}$$

We see that k of Eq. (11) is H independent only in the dirty limit.

Having found $k(H,T)$, one substitutes it in Eq. (6), for which the minimum eigenvalue should be obtained. To proceed, we take the middle plane of the film as $x=0$ and choose the gauge $A_y = xH$, $A_{x,z} = 0$ for the field $\mathbf{H} = H\hat{\mathbf{z}}$.

The nucleation problem near T_c has been studied thoroughly by Fink and Schultens for the field-independent ξ_{GL}.[8] They proved that under usual GL boundary condition, $\Pi_x \Delta(\mathbf{r}) = 0$, for a "thin enough" film, persistent current lines are parallel to the film's plane surfaces, and Δ depends only upon the transverse coordinate x. The field dependence of k notwithstanding, our Eq. (6) is formally identical to the linearized GL equation used in Refs. 8 [the latter coincides with Eq. (1) for $T \to T_c$]. Therefore, the explicit condition obtained in Ref. 8 for the thickness d of a "thin enough" film, $d < 1.84\xi_{GL}$, can be directly translated in our problem as

$$|kd| < 1.84 . \tag{13}$$

In thicker films, vortices start to nucleate, solutions F of Eq. (6) depend on both x and y, and the problem becomes more complicated.

Under restriction (13) and for the boundary condition $\Pi_x F = F'(\pm d/2) = 0$ (we shall comment on this condition below), Eq. (6) reads as

$$F'' - q^4 x^2 F = k^2 F , \tag{14}$$

or, in the dimensionless form,

$$F''(s) - s^2 F(s) = -\eta F(s), \quad s = qx, \quad \eta = -k^2/q^2 . \tag{15}$$

The eigenvalue η is obtained by solving Eq. (15) and imposing the boundary conditions:[6]

$$(1-\eta)\,{}_1F_1\left[\frac{5-\eta}{4}, \frac{3}{2}, s_0^2\right] = {}_1F_1\left[\frac{1-\eta}{4}, \frac{1}{2}, s_0^2\right], \quad s_0 = \frac{qd}{2} , \tag{16}$$

where ${}_1F_1$'s are confluent hypergeometric functions. This equation gives the nucleation field as a function of d at any temperature.

Near T_c one expects $q^2 \propto H \propto |T_c - T|^{1/2}$, while $k^2 \propto |T_c - T|$. Then both $\eta = -k^2/q^2$ and s_0^2 behave as $|T_c - T|^{1/2}$. Kummer's series[9] for the functions ${}_1F_1$ in Eq. (16) converge rapidly and one can truncate them at the first nontrivial terms:

$$(1-\eta)\left[1 + \frac{5-\eta}{6} s_0^2\right] = 1 + \frac{1-\eta}{2} s_0^2 . \tag{17}$$

Keeping only terms of the order $|T_c - T|^{1/2}$, i.e., neglecting ηs_0^2, one obtains $s_0^2 = 3\eta$ or

$$q^4 = (2\pi H/\phi_0)^2 = -12k^2/d^2 . \tag{18}$$

[The result is the same if one retains terms ηs_0^2 and s_0^4 of the order $|T_c - T|$. Moreover, a numerical solution of Eq. (16) shows that Eq. (18) holds within less than 3% accuracy up to $\eta = \frac{1}{3}$ or $s_0 = 1$.] Thus, the assumption $q^4 \propto k^2 \propto |T_c - T|$ is in fact justified. Equation (18) coincides with the known GL result,[8,10]

$$(2\pi H/\phi_0)^2 = 12/d^2 \xi_{GL}^2 , \tag{19}$$

only if one replaces $-k^2(H,T)$ in (18) with ξ_{GL}^{-2}. However, in general parameter k^2 itself depends upon H, so that Eq. (18) gives $H(T)$ only implicitly. To find the nucleation field in the GL domain, one substitutes $k^2(H,T)$ of Eq. (11) in (18) and solves for H:

$$\left[\frac{2\pi H}{\phi_0}\right]^2 = -\frac{12k^2(0,T)}{d^2 - 7.2\gamma(\lambda) l^2} . \tag{20}$$

This coincides with Eq. (19) only in the dirty limit. For any nonvanishing l the slope of $H^2(T)$ at T_c is larger than that predicted in Eq. (19).

The denominator in Eq. (20) changes sign at a critical thickness d_c such that

$$d_c^2 = 7.2\gamma(\lambda) l^2 . \tag{21}$$

The value of d_c increases from $2.68l$ for $\lambda \gg 1$ up to the clean limit $2.62(\hbar v/2\pi T_c)$. The graph of d_c in units $\hbar v/2\pi T_c$ as a function of the impurity parameter λ is given in Fig. 1. For $d > d_c$ the curve $H^2(T)$ is situated in the domain $T < T_c$, where $k^2(0,T)$ is negative. For

$$d < d_c \tag{22}$$

there are no solutions of Eq. (20) for $T < T_c$; the curve $H(T)$ starts at T_c and bends to higher temperatures: $H \propto (T - T_c)^{1/2}$ as shown in Fig. 2. Thus, the condition (22) is a criterion for the anomalous phase boundary to occur.

The prediction just made, for thin enough and sufficiently clean films, implies that the phase boundary for these films can have a shape shown in Fig. 2, cases (b) and

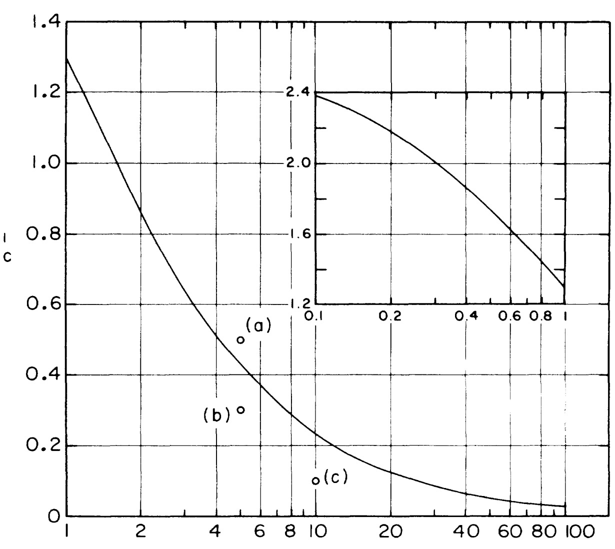

FIG. 1. Critical thickness d_c' evaluated with the help of Eqs. (21) and (11), in units $\hbar v/2\pi k_B T_c$ versus impurity parameter $\lambda = \hbar v/2\pi k_B T_c l$. The condition for the anomalous phase boundary to occur, $d < d_c$, is met for films with normalized thickness d' and effective λ situated under the curve $d_c'(\lambda)$; this is the case in examples (b) and (c). The phase boundary for films with (d', λ) above the curve, as in the case (a), is "normal" with no critical temperature enhancement. Particular positions of points (a), (b), and (c) correspond to parameters given later in the text and in Table I. The inset shows $d_c'(\lambda)$ for $0.1 < \lambda < 1$.

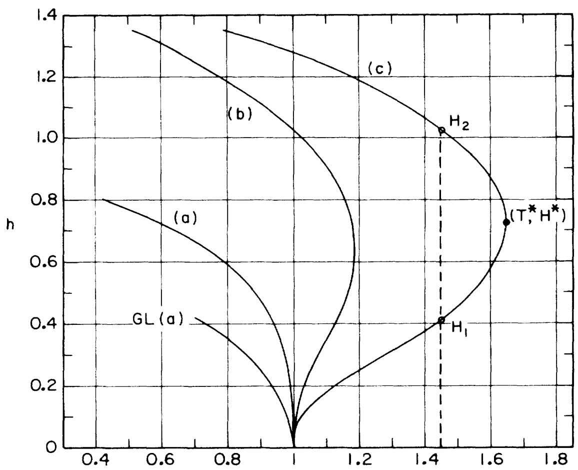

FIG. 2. Phase diagrams of thin films evaluated as described in Sec. IV. The reduced field $h = 2\pi l^2 H/\phi_0$ is plotted against the reduced temperature $t = T/T_c$. The cases (a), (b), and (c) are characterized in Table I. In all cases $\hbar v/2\pi k_B T_c = 1000$ Å. The criterion $d < d_c$ is satisfied for films (b) and (c). In the situation (a), $d > d_c$ and the phase boundary behaves "normally;" however, the slope dh^2/dt at $t = 1$ and $h = 0$ is larger than that obtained from the GL equation (19).

(c). In particular, it would mean that the critical temperature, $T_c(H)$, of a film can be enhanced by applying a parallel magnetic field (which should not be too large). Then, some temperature, T^*, should exist at which the curve $H(T)$ turns over to the usual behavior (see Fig. 2). In the domain (T_c, T^*) function $H(T)$ is double valued. At a constant T in this domain the superconductivity being absent in zero field, should occur at a field H_1 and disappear again at some $H_2 > H_1$. This type of behavior of the phase boundary $H(T)$ does not violate any basic physical requirement. In fact, some magnetic structures show "field-induced superconductivity."[11]

We present now a qualitative argument which shows that the effect described is a direct consequence of the H dependence of the coherence length. Let us start with an observation that Eq. (14) is a Schrödinger-type equation. In zero field we have $-F'' = \varepsilon_0 F$ with $\varepsilon_0 = -k^2(0,T)$ being the "energy eigenvalue." Under the condition $F'(\pm d/2) = 0$, the solution is $F = F_0 = \text{const}$ and $k^2(0,T) = 0$; this happens at $T = T_c$. When a small field is applied, the coherence length becomes shorter: $\xi^2(H,T) = \xi^2(0,T) - \alpha^2 H^2$ with a positive constant α^2 (the first correction due to the field must be even in H). This translates into $-k^2(H,T) = -k^2(0,T) + L^2 q^4$ with some positive material-dependent constant L^2. Substitute this in Eq. (14) and rearrange terms to obtain $-F'' + q^4(x^2 - L^2)F = -k^2(0,T)F$. In a small field the "potential," $V = q^4(x^2 - L^2)$, may be treated as a perturbation so that the new "energy" $\varepsilon = \varepsilon_0 + \langle V \rangle$. This yields

$$-k^2(0,T) = -k^2(0,T_c) + F_0^2 d q^4 (d^2 - 12L^2)/12 .$$

Now, normalize the unperturbed "wave function," $F_0^2 d = 1$, rename $12L^2$ as d_c^2, and recall that $k^2(0,T_c) = 0$ to obtain the main result given in Eq. (20). One can say now that the origin of the change in the phase boundary considered here lies in a change of the eigenvalue for Eq. (6) as, e.g., in the problem of the surface nucleation field $H_{c3}(T)$ as compared to $H_{c2}(T)$. The only new, though essential, information we bring in the problem is the field dependence of the coherence length.

Reservations might be expressed as to validity of the quasiclassical formalism in films for which the thickness is on the order of the mean free path or of the zero-temperature coherence length (in the clean case). The very presence of sharp film surfaces might be a problem for the quasiclassical method which is valid, strictly speaking, only for spatial variations slow with respect to k_F^{-1}. In this context the question arises whether or not the boundary condition $F'(\pm d/2) = 0$ used above is the right one. To estimate how sensitive the effect described might be to boundary conditions, perhaps the most severe one, $F(\pm d/2) = 0$, was tested (see Appendix A). Although the expression for d_c came out different and more restrictive than Eq. (21), there is still a "window" of λ's and d's where the effect should occur.

Another remark should be made with respect to d_c's value in a clean film. Even for a low concentration of scatterers in the "bulk" of a thin film, the surface scattering puts the thickness d as an approximate upper limit for the effective mean free path, unless the surfaces are ideally plane and specular. Consequently, more realistic estimate for d_c in a clean film can be obtained from Eq. (21) with l replaced by d:

$$(d_c/d)^2 = 7.2\gamma(\lambda(d)), \quad \lambda(d) = \hbar v/2\pi T_c d . \tag{23}$$

Numerical estimate of λ at which γ of Eq. (11) equals 1/7.2, yields $d_c = 1.6(\hbar v/2\pi T_c)$. Thus, though the surface roughness reduces the numerical factor in d_c from 2.6 of the specular plane surface to about 1.6, it does not suppress the effect altogether.

The evaluation of the slope of $H^2(T)$ at T_c provides only an indication of a possible critical temperature enhancement, $T^*(H) - T_c(0)$. To calculate this enhancement one should be able to evaluate the sum S of Eq. (7) out of the domain $T \to T_c$ and $H \to 0$. The difficulty of this calculation lies primarily in the formal character of series (7) which converges, in fact, only for a few specific values of parameters involved. The quantity S has a broader domain of application than just in the thin film problem. One might be interested in evaluation of $\xi(H,T)$ and, therefore, of $S(H,T)$ in a wide domain of the plane (H,T) while considering, e.g., various proximity systems or superconducting fluctuations in the normal phase. An integral representation of S is derived in Sec. III; the reader interested only in the result of this rather formal derivation, might skip the text up to Eq. (31).

III. INTEGRAL REPRESENTATION OF S

The function S for a bulk type-II superconductor (where the phase transition occurs at H_{c2}) is given by an integral (4). It also can be represented by a formal (divergent) power series given in Eq. (4). The generalization of

S, valid for finite samples or proximity systems where the second-order transition may occur away from $H_{c2}(T)$, is obtained only in terms of a formal power series (7). Our purpose now is to cast the series (7) into a well defined integral.

Let us start with rearranging the double series (7) into a single sum. For convenience, let us introduce a new variable

$$\sigma=(k^2/q^2-1)/2 \ . \tag{24}$$

Then the product in (7) can be written as $(2q^2)^m(\sigma+1)_m$, where $(\sigma+1)_m=(\sigma+1)(\sigma+2)\cdots(\sigma+m)$. Instead of independent summations over m and j in Eq. (7), one can sum up over $\mu=m+j$ from 0 to ∞ and over m from 0 to μ. Then S assumes the form

$$S(u,\sigma)=\sum_{\mu=0}^{\infty}\frac{(-1)^{\mu}\mu!}{2\mu+1}u^{\mu}\,{}_2F_1(-\mu,\sigma+1;1;2)$$
$$u=l^2q^2/\beta^2\ , \tag{25}$$

where the hypergeometric function ${}_2F_1$ is, in fact, a polynomial [see Eq. (15.4.1) in Ref. 9].

The idea behind the following manipulations is to convert the sum (25) into an integral with the help of the relation

$$\sum_{\mu=0}^{\infty}\mu!z^{\mu}=\mathrm{Re}\int_0^{\infty}d\zeta\frac{e^{-\zeta}}{1-\zeta z}\ , \tag{26}$$

where the left-hand side (lhs) is obtained formally from the rhs by expanding $(1-\zeta z)^{-1}$ in the power series and by integrating over ζ.[12] (The divergent sum such as this is called sometimes "Borel-summable.") For positive z, the integral at the right has, in fact, an imaginary part, $\pm(i\pi/z)e^{-1/z}$, originating in a certain way chosen to avoid the pole $\zeta=1/z$. We discard this part (by taking the real part of the integral), because the sum at the lhs is formally real.

In order to get rid of the factor $(2\mu+1)^{-1}$ in the sum (25), we call $v=l/\beta$ (or $u=v^2q^2$) and introduce an auxiliary quantity

$$S_1=\frac{\partial}{\partial v}(vS)=\sum_{\mu=0}^{\infty}\mu!(-u)^{\mu}\,{}_2F_1(-\mu,\sigma+1;1;2)\ . \tag{27}$$

We now replace ${}_2F_1$ by its integral representation [see Eq. (5.3.20) of Ref. 13]:

$${}_2F_1(-\mu,\sigma+1;1;z)=(2\pi)^{-2}e^{-i\pi(\sigma+1)}\Gamma(\sigma+1)\Gamma(-\sigma)\times\oint_C(t-z)^{-\sigma-1}t^{\sigma}(1-t)^{\mu}dt\ , \tag{28}$$

where C is Pochhammer's contour which encircles the branch points of the integrand at $t=0$ and $t=z$ twice in opposite directions. [One could use a "simpler" representation, Eq. (15.3.1) of Ref. 9, however, paying a price in a certain restriction imposed upon σ.] The representation (28) serves well our purpose: after changing the order of summation and integration in Eq. (27), we can lump the factors u^{μ} and $(1-t)^{\mu}$ together in $[u(1-t)]^{\mu}$ and use identity (26). Thus, we have eliminated the summation; instead we now have S_1 represented by a double integral $\oint dt\int d\zeta\ldots$. Further, we change the order of integrations and apply once more the representation (28) to convert the contour integral back into a hypergeometric function:

$$S_1=\mathrm{Re}\int_0^{\infty}d\zeta\frac{e^{-\zeta}}{1+\zeta u}\,{}_2F_1\left[1,\sigma+1;1;\frac{2\zeta u}{1+\zeta u}\right]\ . \tag{29}$$

This is simplified readily with the help of Eq. (15.3.5) of Ref. 9 to

$$S_1=\mathrm{Re}\int_0^{\infty\pm i0}d\zeta e^{-\zeta}\frac{(1+\zeta u)^{\sigma}}{(1-\zeta u)^{\sigma+1}}\ . \tag{30}$$

Thus, we succeeded in converting the sum (27) into a single integral. We added $\pm i0$ in the upper limit of integration to specify the upper or lower banks of the branch cut along the segment $(1/|u|,+\infty)$ of the real axis at the complex plane ζ. The integrals along the upper and lower banks of the cut are complex conjugate, so that the result (30) is unique.

Finally, we recover the quantity of interest, $S(u,\sigma)$, recalling its relation to S_1 given in Eq. (27). After a straightforward algebra (see Appendix B), we obtain

$$S(u,\sigma)=\sqrt{\pi}\,\mathrm{Re}\int_0^{\infty\pm i0}ds\frac{(1+us^2)^{\sigma}}{(1-us^2)^{\sigma+1}}\mathrm{erfc}s\ , \tag{31}$$

where $\mathrm{erfc}s=(2/\sqrt{\pi})\int_s^{\infty}\exp(-z^2)dz$.

The integral representation of S just obtained reduces to known expressions in limits for which the function S is given in a closed form. One of these limits is the case of the bulk upper critical field where $k^2=-q^2$ and therefore $\sigma=-1$. The integrand in Eq. (31) then simplifies and we obtain the result (4) just integrating by parts.

Another limit to check is the case of zero field for which $u=q^2l^2/\beta^2\to 0$, $\sigma\to+\infty$ for positive k^2, while $\sigma u\to(kl/\beta)^2/2$. This corresponds to $T>T_c$; the quantity S of this case is used to evaluate the "pair penetration depth" into the normal phase. In this limit the numerator of the integrand (31) reduces to $\exp(k^2l^2s^2/2\beta^2)$ [since $(1+1/z)^z\to e$, when $z\to\infty$]. The denominator goes to $\exp(-k^2l^2s^2/2\beta^2)$, and after integration[14] over s we recover Eq. (8).

The representation (31) shows that the function S satisfies a symmetry relation:

$$S(u,\sigma)=S(-u,-\sigma-1)\ . \tag{32}$$

This is a manifestation of the obvious symmetry with respect to the change of the field direction to the opposite: if $H_z\to-H_z$, then $q^2\to-q^2$, $u\to-u$, and $\sigma+1\to-\sigma$ [see Eqs. (7), (24), and (25) for definitions of q, σ, and u]. In particular, this symmetry means that in the expansion (7) of S there are no terms with odd powers of q^2.

In conclusion of this section, one can verify that the integral (31) can be represented indeed by the series (7). This is done in Appendix C by expanding formally the integrand (31) in powers of us^2 and then by integrating over s.

TABLE I. Values of d_c, T^*/T_c, and H^* are evaluated for three films with effective mean free paths l and thicknesses d of the same metal with $\hbar v/2\pi k_B T_c = 1000$ Å.

Case	l (Å)	λ	d (Å)	d_c (Å)	T^*/T_c	H^* (kgs)	$\lvert kd \rvert$ at T^*
(a)	200	5	500	434			
(b)	200	5	300	434	1.17	5.2	1.5×10^{-2}
(c)	100	10	100	236	1.65	24.0	3.9×10^{-3}

IV. NUMERICAL RESULTS

In order to write the result (31) in an explicitly real form we separate the integration domain in two:

$$\frac{S}{\sqrt{\pi}} = \int_0^{1/\sqrt{u}} ds \frac{(1+us^2)^\sigma}{(1-us^2)^{\sigma+1}} \operatorname{erfc}(s) - \cos(\pi\sigma) \int_{1/\sqrt{u}}^{\infty} ds \frac{(1+us^2)^\sigma}{(us^2-1)^{\sigma+1}} \operatorname{erfc}(s) \; . \tag{33}$$

We now note that not all possible values of σ are relevant for the thin-film problem. To determine the relevant domain we integrate Eq. (14) over the film $(-d/2 < x < d/2)$ and take boundary condition $F'(\pm d/2)=0$ into account to obtain: $q^4\langle x^2 F\rangle = -k^2\langle F\rangle$. Therefore, everywhere at the nucleation curve $H(T)$, k^2 must be negative. In other words, for a thin film

$$\sigma < -\tfrac{1}{2} \tag{34}$$

[see Eq. (24)]. In particular, this condition means that singularities in integrands of Eq. (33) are integrable.

Having in mind the numerical work, we change the integration variables in (33) from s to $y = s\sqrt{u}$ in the first integral and to $y=(s\sqrt{u}\,)^{-1}$ in the second. Then Eq. (33) assumes the form

$$S(u,\sigma) = \left[\frac{\pi}{u}\right]^{1/2} \int_0^1 dy \frac{(1+y^2)^\sigma}{(1-y^2)^{\sigma+1}} \times [\operatorname{erfc}(y/\sqrt{u}\,) - \cos(\pi\sigma)\operatorname{erfc}(y\sqrt{u}\,)^{-1}] \; . \tag{35}$$

This integral can be evaluated numerically.

We have now all the necessary components for calculation of the nucleation field $H(T)$ for a thin film. The calculation proceeds as follows. For a film of a given thickness d and an effective mean free path l, in a given field H, we first solve Eq. (16) to find the corresponding eigenvalue $\eta = -k^2/q^2$.[15] Then the value of σ is obtained from Eq. (24) and the integral (35) is evaluated for different Matsubara frequencies ω [the latter enter $S(u,\sigma)$ via $u = l^2q^2/(1+2\omega\tau)^2$]. Further we proceed with solution of the self-consistency equation (3). The summation in (3) is extended until a certain convergence criterion is met. Then a check is performed on whether or not a particular (H,T) solves Eq. (3). If not, one goes to the next temperature $T+\Delta T$ with a certain increment ΔT, until the root (H,T) is found.

The numerical results are shown in Fig. 2 for a film with $\hbar v/2\pi T_c = 10^3$ Å for three different sets [(a),(b),(c)] of d's and l's given in Table I. The corresponding values of d_c's are obtained with the help of Eq. (21) or from the graph, Fig. 1. In case (a) the criterion (22) is not satisfied and the phase boundary behaves "normally;" we also show for comparison the curve obtained with the help of GL formulas (19) and (12). For the parameters chosen, the slope dH^2/dT at T_c and $H=0$ exceeds the slope of the GL curve by about a factor of 5. In case (b), $d<d_c$, the phase boundary is anomalous. Case (c) corresponds to a situation when the "bulk" mean free path exceeds the thickness, so that the effective l is approximated by d. Also, we show in Table I the ratio T^*/T_c and the field H^* at which the critical temperature is maximum.

During the calculation we monitor the values of $\lvert kd \rvert$. It is needed to assure that we are within the domain (13) $(\lvert kd \rvert < 1.84)$, where Eq. (16) for the eigenvalue holds; although we show in the table only $\lvert kd \rvert$ at (T^*,H^*), as a matter of fact this condition is satisfied along all curves presented.

V. DISCUSSION

As we pointed out in Sec. III, application of the quasiclassical method to thin films is still to be justified. Also, it is not at all clear, what kind of boundary conditions should be used if the method is applied.

One can argue, on the other hand, that the same doubts can be expressed with respect to the GL theory, which is, in fact, derived from the microscopic theory in a quasiclassical approximation (see, e.g., Ref. 16). It is generally accepted that the standard GL boundary condition [in our problem it reads as $\Delta'(\pm d/2)=0$] is basically correct, unless the surface has some intrinsic properties different from the bulk. Equation (19) for the nucleation field near T_c is obtained from the GL theory subject to this boundary conditions.[10] The major prediction of this equation, namely, $(T_c - T)^{1/2}$ dependence of H, is well established experimentally.

Given this success of the GL theory, one might expect the more general Eilenberger quasiclassical theory [subject to boundary condition $F'(\pm d/2)=0$] to work equally well at least in the domain near $T=T_c$ and $H=0$. In this domain the theory predicts an anomalous slope dH^2/dT if the condition (22) is met. The prediction calls for experimental verification.

In order to observe the T_c enhancement one should prepare a film which meets criterion (22). As Eq. (21) shows, the critical thickness d_c normalized by $\hbar v/2\pi T_c$, is a universal function of the impurity parameter λ (Fig. 1). The condition, $d<d_c$, for the anomalous phase boun-

dary to occur, is easier to satisfy in materials with low T_c's and high Fermi velocities or, in other words, with large zero-temperature BCS coherence length. (For example, good quality indium films with $d<50$ Å can be prepared,[17] with no suppression in T_c; in fact, T_c of In films might be higher than in the bulk.[18]) Most of these metals are type-I superconductors where the bulk phase transition in the field is of the first order. However, in sufficiently thin films made of intrinsicly type-I metals, the phase transition is of second order if $d<2.24\Lambda$ with Λ being the magnetic field penetration depth (see, e.g., Tinkham's book in Ref. 10). This condition was obtained near T_c and as such cannot be extrapolated far from the point $T=T_c$, $H=0$; it is enough to mention that all known values of Λ are obtained in small fields. Thus, although type-I materials seem to be promising, it is difficult to delineate the domain where our theory is valid. On the other hand, strong suppression of the effective mean free path in thin films might convert them in type II. We would like to stress, however, that if one succeeds in fabricating a film of whatever type superconductor with $d<d_c$, the slope of $H^2(T)$ at $T=T_c$ and $H=0$ should be positive, i.e., the phase boundary should be anomalous.

Still, given the uncertainty with the method's applicability to thin films, it remains to be seen whether our theory provides a right estimate for the whole curve $H(T)$ and, in particular, for the T_c enhancement. Questions of fluctuations and the transition width along the anomalous phase boundary are out of the scope of our paper. We should point to yet another shortcoming of our theoretical model. Namely, we do not know "how parallel" the field should be to the film.[19] Or, in other words, how large the normal component of the field with respect to the parallel one could be for the anomalous phase boundary to survive. In the absence of a quantitative estimate for the maximum allowable spread in field directions, we resort to the notion, that had the phase boundary in the parallel field been unstable with respect to small field perturbations normal to the film, even the usual $(T_c-T)^{1/2}$ dependence of H could not be observed.

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APPENDIX A

Boundary condition

$$F(\pm d/2)=0 \tag{A1}$$

can be interpreted physically as a result of a strong pair breaking at the film surfaces. In particular, the zero-field critical temperature T_c of a thin film is suppressed with respect to the critical temperature T_{c0} of the bulk material. The suppression is evaluated easily for $H=0$: the solution $F=F_0\cos|k|x$ of Eq. (14) satisfies condition (A1) if

$$|k(0,T_c)|=\pi/d \tag{A2}$$

(note: $k=0$ at T_{c0}, not at T_c). Because $\xi(0,T)$ is minimum at $T=0$, superconductivity is totally suppressed in a film if

$$d<d_{\min}=\pi\xi(0,0)\ . \tag{A3}$$

With the field present, the even solution of Eq. (15), $\exp(-s^2/2)\,{}_1F_1((1-\eta)/4,1/2,s^2)$, yields under condition (A1) an equation for the eigenvalue η:

$${}_1F_1((1-\eta)/4,1/2,s_0^2)=0,\quad s_0=qd/2\ . \tag{A4}$$

We are interested in the phase boundary near T_c for $H\to 0$. In this domain $\eta=-k^2/q^2\to\infty$. Note the difference with the situation near T_{c0} considered in the text: there $\eta\to 0$ because $k\to 0$ faster than q. The first positive root of Eq. (A4) is[20]

$$s_0^2=\frac{\pi^2}{4\eta}\left[1+\frac{\pi^2-6}{12\eta^2}\right]+O(\eta^{-4})\ . \tag{A5}$$

With $\eta=-k^2/q^2$ this translates in

$$-\frac{k^2d^2}{\pi^2}-1=\frac{(\pi^2-6)q^4}{12k^4}\ . \tag{A6}$$

For the sake of simplicity we consider the moderately dirty case in which $k^2(H,T)=k^2(0,T)-3l^2q^4/5$ [set $\gamma=1$ in Eq. (11)]. We are interested in the curve $H(T)$ near T_c, where $k^2(0,T)=-\pi^2/d^2+k^{2\prime}(T_c)(T-T_c)$, where $k^{2\prime}(T_c)$ denotes dk^2/dT at T_c. Taking all this into account at the left of Eq. (A6) and replacing k^4 at the right with π^4/d^4, we obtain after simple manipulation:

$$q^4=\frac{12\pi^2k^{2\prime}(T_c)(T-T_c)}{(\pi^2-6)(d_0^2-d^2)},\quad d_0\simeq 4.29l\ . \tag{A7}$$

This result has the same structure as Eq. (20). For $d<d_0$ the curve $H(T)$ bends at T_c to higher temperatures [note that $-k^{2\prime}=(\xi^{-2})'<0$]. Thus, under boundary condition (A1), the phase boundary is anomalous if $d_{\min}<d<d_0$.

APPENDIX B

Using Eqs. (27) and (30) we obtain

$$vS=\mathrm{Re}\int_0^v dv\int_0^\infty d\zeta e^{-\zeta}\frac{(1+\zeta q^2v^2)^\sigma}{(1-\zeta q^2v^2)^{\sigma+1}}\ . \tag{B1}$$

Replace here ζ with a new variable $z=q^2v^2\zeta$, change the order of integrations and integrate over v:

$$vS=\frac{\sqrt{\pi}}{2q}\mathrm{Re}\int_0^\infty\frac{dz}{\sqrt{z}}\frac{(1+z)^\sigma}{(1-z)^{\sigma+1}}\mathrm{erfc}\frac{\sqrt{z}}{qv}\ . \tag{B2}$$

This yields Eq. (31) after yet another substitution, $s=\sqrt{z}/qv$.

APPENDIX C

Start with a transformation

$$\frac{(1+us^2)^\sigma}{(1-us^2)^{\sigma+1}} = \left[\frac{1-us^2}{1+us^2}\right]^{-\sigma-1} \frac{1}{1+us^2}$$
$$= \left[1-\frac{2us^2}{1+us^2}\right]^{-\sigma-1} \frac{1}{1+us^2}$$
$$= \sum_{m=0}^{\infty} \begin{bmatrix} -\sigma-1 \\ m \end{bmatrix} \frac{(2us^2)^m}{(1+us^2)^{m+1}}$$
$$= \sum_{m,n=0}^{\infty} \begin{bmatrix} -\sigma-1 \\ m \end{bmatrix} \begin{bmatrix} -m-1 \\ n \end{bmatrix} \times 2^m u^{m+n} s^{2m+2n} .$$

Now substitute this in Eq. (31), integrate over s by parts, and use the identity

$$\begin{bmatrix} -\alpha \\ n \end{bmatrix} = \frac{(-1)^n(\alpha)_n}{n!} .$$

The result coincides with the sum (7). Note that both S^+ and S^- have identical Borel series (7) [S^+ and S^- are the integrals (31) taken along the upper and lower banks of the branch cut]. Hence the same is true for $S=(S^+ + S^-)/2$.

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