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Surface term in the superconductive Ginzburg-Landau free energy: Application to thin films

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A new term is added to the Ginzburg-Landau free energy which modifies the boundary condition for the order parameter. The new boundary condition is applied to the case of thin films, where it successfully explains the decrease in the critical temperature observed in samples of Nb, Pb, and Bi. The theory allows for a simple calculation of the response to applied magnetic fields. A microscopic analysis of the new term is given.

When written in normalized units the superconductive Ginzburg-Landau (GL) free energy, in absence of external magnetic fields,[1] reads[2]

$$F_{GL}=(\hbar^2\psi_0^2/2m)\int_V[(-f^2+f^4/2)/\xi^2(T)+(\nabla f)^2]dv\ , \quad (1)$$

where f is the normalized order parameter $f=|\psi|/\psi_0$, ψ_0 the bulk value of the order parameter at zero field, and $\xi(T)$ is the temperature-dependent coherence length. The new term which we add is of the form $\int_S Cf^2\,ds$, where the integral runs over the surface of the superconductor and C is a constant to be discussed later on.

To find the variational equations corresponding to the free energy Eq. (1) plus the added new term, we calculate the first variation with respect to f and find

$$\delta F\sim\int_V[(-f+f^3)/\xi^2(T)-\nabla^2 f]\delta f\,dv + \int_S(\nabla f\cdot\hat{s}+Cf)\delta f\,ds\ , \quad (2)$$

where $\hat{s}$ is the unit vector outgoing the surface and δf the variation of f. From the condition $\delta F=0$ we obtain

$$\xi^2(T)\nabla^2 f=-f+f^3\ , \quad (3a)$$

plus the boundary condition (BC)

$$\nabla f\cdot\hat{s}|_s=-Cf|_s\ . \quad (3b)$$

It is seen that the GL equation itself is not modified, but that the boundary condition is altered as shown in Eq. (3b). The ordinary BC corresponds to $C=0$.

To analyze the consequences of the new term we discuss briefly the case of a thin film of thickness d. Choosing the coordinate system such that the film is parallel to the xy plane and extends from $z=-d/2$ to $z=d/2$, Eqs. (3) read

$$\xi^2(T)f''=-f+f^3\ , \quad (4a)$$

$$f'(\pm d/2)=\mp Cf(\pm d/2)\ . \quad (4b)$$

These equations can be solved exactly.[3] But since we are only interested in the critical temperature T_d of the film, it is enough to solve Eqs. (4) to first order in f. This gives

$$f=f_0\cos[z/\xi(T)]\ . \quad (5)$$

The boundary condition fixes the critical temperature T_d of the film through

$$\tan[d/2\xi(T_d)]=C\xi(T_d)\ . \quad (6)$$

For $d/\xi(T_d)\ll 1$ we can write this as

$$d/2C=\xi^2(T_d)\ , \quad (7)$$

which, using

$$\xi^2(T)=\xi^2(0)T_c/(T_c-T)\ ,$$

where T_c is the bulk critical temperature, reduces to

$$T_d=T_c[1-2C\xi^2(0)/d]\ . \quad (8)$$

Using Eq. (7), the validity condition for Eq. (8) can be written as $Cd\ll 1$, and since, as we shall see later, $C\simeq(10^4\ \text{Å})^{-1}$, Eq. (8) is valid in the whole region of interest for thin films.

We can define a critical thickness d_m $[=2C\xi^2(0)]$ as the value of d for which Eq. (8) gives $T_d=0$. Thus we can write $T_d=T_c(1-d_m/d)$. This shows that the new term in the free energy gives a simple explanation for the observed[4–6,10] linear dependence of T_d on $1/d$.

In Fig. 1 we plot the data of Wolf, Kennedy, and Nisenoff[4] for T_d of thin films of niobium and the fit of our results (full line). From this we obtain $d_m=36$ Å. The deviation of the last four points[9] corresponding to ultrathin films is discussed below in connection with the microscopic

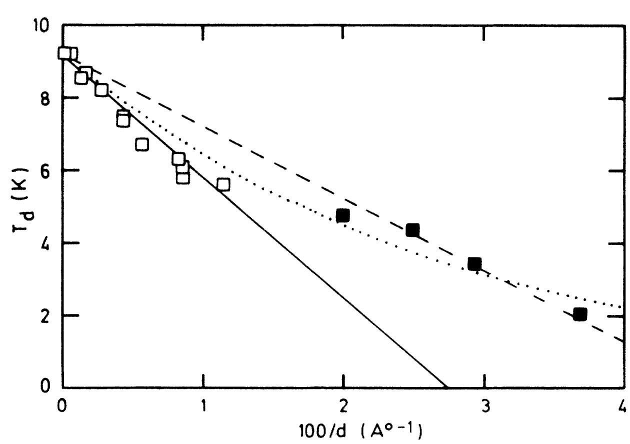

FIG. 1. T_d as function of $1/d$. □, ■: experimental data for Nb after Wolf *et al.* (Ref. 4). Full line: Eq. (6) with $d_m=36$ Å; dashed line: fit of Eq. (8) to the last four points (Ref. 9) of Wolf *et al.* (Ref. 4) ($d_m=22$ Å); dotted line: Cooper's law (Ref. 4) ($d_m=36$ Å).

analysis of C. A fit to the data of Mayadas *et al.*[6] gives $d_m = 30$ Å.

In Fig. 2 we show the fit to the data of Strongin *et al.*[5] for Bi ($d_m = 12$ Å) and Pb. In this last case we obtain $d_m = 20$ Å or $d_m = 8$ Å, according to whether we use the data corresponding to the dark triangles or dark points in Fig. 6 of Ref. 5. In fact, Eq. (8) gives a good fit to the ten series of data for Pb presented by Strongin *et al.*,[5] each characterized by a different substratum or deposition method, changing d_m from series to series.

At this point we want to mention that Eq. (8) can also be obtained directly from the free energy to second order in f, assuming $f = f_0 = \text{const}$,

$$F \sim f_0^2[-d/\xi^2(T) + 2C] , \tag{9}$$

and looking for the point at which $F = 0$.

When a magnetic field is applied to the sample the free energy, up to the second order in f, changes to

$$F = \frac{\hbar^2\psi_0^2}{2m}\left(\int_V [-f^2/\xi^2(T) + (\nabla f)^2 + \mathbf{Q}^2 f^2]dv + \int_S Cf^2\,ds\right) . \tag{10}$$

The linearized GL equation is now

$$\xi^2(T)\nabla^2 f = -f + \xi^2(T) f \mathbf{Q}^2 , \tag{11a}$$

with the boundary conditions

$$\mathbf{Q}\cdot\hat{\mathbf{s}}|_s = 0 , \tag{11b}$$

$$\nabla f \cdot \hat{\mathbf{s}}|_s = -Cf|_s . \tag{11c}$$

Here $\mathbf{Q}$ is the velocity field of the superconducting electrons, given by $\mathbf{Q} = (\nabla\varphi - 2\pi\mathbf{A}/\phi_0)$, where φ is the phase of the order parameter, $\mathbf{A}$ the vector potential, and ϕ_0 the flux quantum.

The boundary condition Eq. (11b) assures as usual that no currents leave the superconductor and Eq. (11c) must be used to find the exact mean-field solution of the problem by means of Eq. (11a).

Let us discuss briefly the case of a magnetic field normal to the film. We have $\mathbf{Q} = \rho h \hat{\mathbf{e}}_\varphi/2$ where ρ is the radial coordinate and $\hat{\mathbf{e}}_\varphi$ the unit vector perpendicular to the directions of ρ and z. In this case, Eq. (11a) has the solution

$$f = f_0\cos[\alpha z/\xi(T)]\exp[-\rho^2(1-\alpha^2)/4\xi^2(T)] , \tag{12}$$

with

$$\tan[\alpha d/2\xi(T)] = C\xi(T)/\alpha . \tag{13}$$

The perpendicular critical field is given by

$$h_\perp = (1-\alpha^2)/\xi^2(T) . \tag{14}$$

In the same limit in which Eq. (8) was obtained, Eq. (13) can be reduced to $\alpha^2/\xi^2(T) = 2C/d$, and accordingly

$$h_\perp = 1/\xi^2(T) - 2C/d = 1/\xi^2(T) - 1/\xi^2(T_d) = (T_d - T)/\xi^2(0)T_c . \tag{15}$$

The case of an applied field parallel to the film is more complicated, but for $d << \xi(T)$ the result can be obtained by the same procedure as used in Eq. (9).

In this case, $\mathbf{Q} = hz\hat{\mathbf{e}}_y$ ($\hat{\mathbf{e}}_y$ is the unit vector along the y axis), and with $f = f_0 = \text{const}$, we have from Eq. (10)

$$F \sim f_0^2[-d/\xi^2(T) + h^2d^3/12 + 2C] , \tag{16}$$

and thus,

$$h_\parallel^2 = (12/d^2)[1/\xi^2(T) - 2C/d] = [12/d^2\xi^2(0)](T_d - T)/T_c . \tag{17}$$

Comparing this with Eq. (15) we see that the well-known relation $(h_\perp/h_\parallel^2) = (d^2/12)$ is conserved.

From Eq. (15) we see that $\partial h_\perp/\partial T = -1/\xi^2(0)T_c$, independent of d. Although there are no consistent data over the critical fields of thin films, recent measurements of the total thickness effect in metallic multilayer compounds[7] follow this law.

Defining a renormalized zero temperature coherence length as

$$\xi(0,d) = \xi(0)\sqrt{T_c/T_d} , \tag{18}$$

we can rewrite Eq. (15) as $h_\perp = (1-t)/\xi^2(0,d)$ and Eq. (17) as

$$h^2 = 12(1-t)/d^2\xi^2(0,d) ,$$

where $t = T/T_d$, which leads to the usual form used to plot experimental data.

The microscopic origin of C could be traced to de Gennes's[2] analysis of the derivation of the GL equations made by Gorkov, where he states that the appropriate boundary condition for the superconducting gap [$\Delta(r)$, proportional to f] is

$$\nabla\Delta\cdot\hat{\mathbf{s}}|_s = -C\Delta_s . \tag{19}$$

For a superconducting-insulator (or vacuum) interface (at $z = 0$) he obtains

$$C = (2/L^2)\int_0^\infty dz[\Delta(z)/\Delta_0][1 - N(z)/N_0] , \tag{20}$$

where Δ_0 [$\Delta(z)$] and N_0 [$N(z)$] are the bulk values (at z) of the gap and of the density of states at the Fermi energy. L is the range of the kernel K_0 of the self-consistent equa-

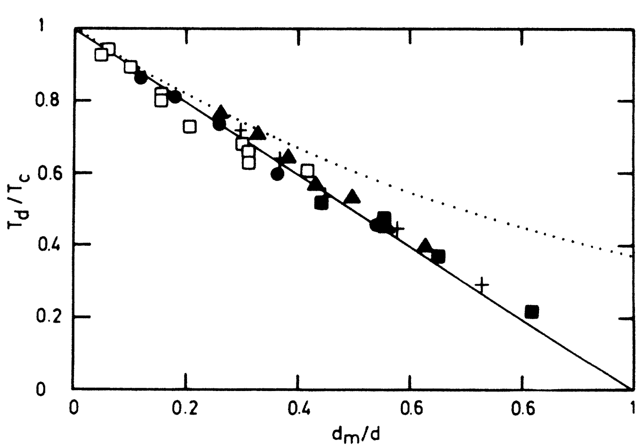

FIG. 2. Universal plot: T_d/I_c vs d_m/d. The full line is Eq. (8) and the dotted line is Cooper's law, Eq. (23). The experimental points are as follows Nb (Ref. 4) = □ ($d_m = 36$ Å) and ■ ($d_m = 22$ Å); Pb (Ref. 5) = ● ($d_m = 8$ Å) and ▲ ($d_m = 20$ Å); and Bi (Ref. 5) = + ($d_m = 12$ Å).

tion for $\Delta(z)$:

$$L^2 = \int K_0(r) r^2 \, dr \simeq 2 N_0 V \xi^2(0) \ , \tag{21}$$

where $N_0 V$ is the bulk interaction potential.

In our case (dirty metal) $\xi(0) = 0.85\sqrt{\xi_0 l}$, with ξ_0 $(= 0.18 \hbar v_f / k_B T_c)$ the size of the Cooper pairs and l the electronic mean free path. The integral Eq. (20) can be estimated to be of the order of the Thomas Fermi screening length a, which in turn is of the order of a lattice parameter, and thus we have

$$C = a / N_0 V \xi^2(0); \quad d_m = 2a / N_0 V \ . \tag{22}$$

For Nb Eqs. (22) give [using[4] $a = 5$ Å, $N_0 V = 0.32$, $\xi(0) = 161$ Å] $C = (1700 \text{ Å})^{-1}$ and $d_m = 31$ Å, in agreement with the value found above. de Gennes[2] estimated C in the clean limit [$\xi(0) \simeq (10^4 \text{ Å})$] to be of the order of $(10^8 \text{ Å})^{-1}$, and thus underestimated its role. In the dirty limit C becomes more important, modifying among other things the ratio (h_{c3}/h_{c2}) for surface superconductivity. In the case of thin films the relevant quantity is d_m, which does not depend on the mean free path [within our simplified calculation, Eq. (22)], and thus even for films of clean material the effect discussed in this paper is present.

The Cooper law,[4,8] commonly used to fit the experimental results for T_d in thin films, can be written

$$T_d = T_c \exp(-d_m/d) \ , \tag{23}$$

where the coefficient d_m is the same as in our Eqs. (8) and (22). Although Eq. (23) has the same origin as our new term in the free energy, i.e., the decrease of the density of states near the surfaces, it is obtained through a proximity effect model (introducing a "nonsuperconductive" surface layer of thickness a). Cooper's law fails to explain the linear dependence of T_d with $1/d$ for small d, and gives the unphysical result that $T_d > 0$ for any d, i.e., even for $d < 2a$. Magnetic field effects are hard to obtain from that model.

Going back to the microscopic expression for d_m [Eq. (22)] and the data of Wolf *et al.*,[4] we can see that Eq. (8) can be made to fit[9] the last four points but with a lower $d_m = 22$ Å (dashed line in Fig. 1). Also in the fit to the data of Strongin *et al.*,[5] d_m changes for the different groups of Pb films. This suggests that the expression for C, and the consequent expression for d_m, are oversimplified. Further theoretical and experimental work will be needed in order to clarify the role of the substratum and the electronic mean free path on C.

The relevant parameter is probably the mean free path,[10] with decreasing d_m for decreasing l. An alternative possibility to explain the changes in d_m could be a change of the bulk interaction potential $(N_0 V)$, but this seems not to be the case since all different groups of a given material extrapolate to the same T_c [please recall $k_B T_c = 1.14 \hbar w_d \exp(-1/N_0 V)$].

In conclusion, we have shown that the new term added to the GL free energy adequately describes the behavior of thin films, including the zero-field transition point and field effects, using either the free energy equation (10) or the ensuing minimization equations (11).

This term (or new boundary condition) has important consequences on the surface critical field of dirty superconductors modifying the 1.7 ratio and should also be of importance in the case of fluctuations in small-size superconductors, where the surface-to-volume ratio is dominant. We are currently working over these points.

Since the GL free energy is widely used in the study of second-order transitions (as superfluid He[4], ferromagnetism, etc.) this new term might be also explored in connection with these systems.

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[1]The added term does not modify the role of the vector potential in the GL equations, and thus we use the free energy without field in order to keep the analysis simple.

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[9]It must be pointed out that the data of Wolf (Ref. 4) correspond to the onset of superconductivity (1% of the resistivity transition) and that the transition width is of the order of 1 K for these thinner four films; so the actual T_d must be something lower than the plotted one. Fluctuation effects could raise T_d over the predictions of the GL equation.

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