Consistent calculation of boundary effects in thin superconducting films*

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A simple model is proposed to treat the quantum size effect in thin superconducting films so as to account for screening of the surface charge, and to thereby provide consistency with the Friedel sum rule for metal surfaces and the constancy of the Fermi level. The original Thompson and Blatt calculation is followed with the additional feature that the overlap integrals for the electron-phonon interaction are only evaluated over the geometrical thickness, which defines the extent of the ion cores even though the electron gas extends beyond the cores. This procedure provides a factor which lowers T_c that is of the order measured in experiments.

INTRODUCTION

Various calculations[1-4] have been made of the effect of the boundary conditions and film size on the superconducting transition temperature T_c for thin films, and of how shape resonances might be observed under appropriate conditions. Recently, the question of the validity of the boundary conditions in films used in earlier calculations has been raised by Allen.[5] It is the purpose of this note to reconsider the previous calculations in terms of more realistic boundary conditions. A result of this calculation is that the envelope curve for the gap with decreasing thickness shows a reduction in T_c (as opposed to previous predictions of an increase in T_c), for the thinnest films, in better agreement with experiment.

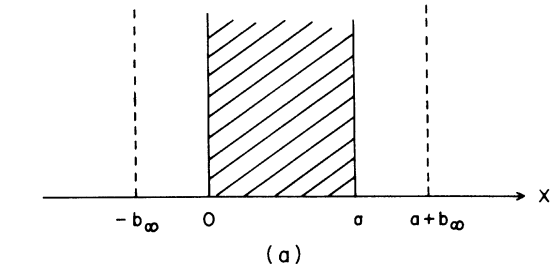
TREATMENT OF THE BOUNDARY

In previous calculations of the T_c of superconducting thin films, the boundary was treated by constructing an infinite wall at the boundaries ($x = 0, a$, Fig. 1) and using sine functions to make the wave function zero at the wall,[1,2] or by making the slopes of the wave function vanish at the boundary,[3] which implies cosine functions. Allen[5] points out that both choices are not realistic since they violate the Friedel sum rule for metal surfaces. With the wave function $\psi(x)$ written in the form

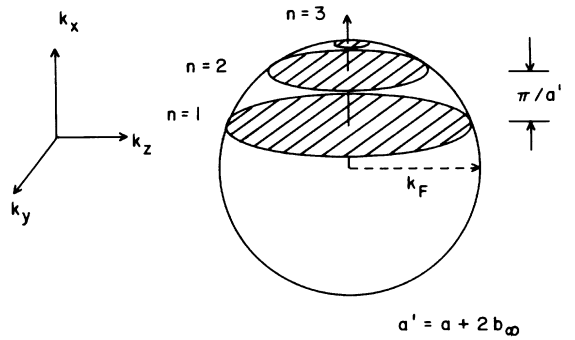
$$\psi(x) \sim e^{ikx} - e^{-2i\eta} e^{-ikx}, \tag{1}$$

the sum rule says that the average phase shift $\langle \eta \rangle$ has to be $\frac{1}{4}\pi$. This result was obtained earlier by Appelbaum and Blount[6] for a thin metallic slab. They also showed that the Fermi momentum k_F is independent of thickness a of the slab to the order of $(1/k_F a)^2$. Here we are going to propose a simple model for size quantization which is consistent with those boundary conditions.

Some years ago, Sugiyama[7] showed that a consistent solution of the charge distribution at the surface of a semi-infinite metallic conductor could be obtained if the geometrical boundary was moved out a distance $b_\infty = 3\pi/8k_{F0}$, where k_{F0} is the bulk Fermi momentum, and an infinite wall was placed



(a)



(b)

FIG. 1. (a) To allow for the leakage of electron wave functions out from the metal surface, the infinite walls are now placed at $x = -b_\infty$ and $a + b_\infty$ instead of at geometric boundaries $x = 0, a$ of the film. (b) Owing to quantization of the k vector in the x direction, the k sphere is degenerated into circular disks in the k_y, k_z plane as shown. In our model, the separation of the disks is π/a', where a' is the "physical" thickness $a + 2b_\infty$.

in this new position. It should be noted that an important part of this calculation is that k_F is not changed by the introduction of a surface. We extend this idea to very thin films and take into account the leakage of electronic wave function across the slab geometric surfaces by placing the infinite walls a distance b_∞ outside the slab, so that the film has a "physical thickness" $a' = a + 2b_\infty$. The wave function is assumed to vanish at the "physical" boundary as in Fig. 1(a), and is given by

$$\psi \sim \sin k_n(x + b_\infty) \sim e^{ik_n b_\infty}(e^{ik_n x} - e^{-2ik_n b_\infty} e^{-ik_n x}), \tag{2}$$

where $k_n = n\pi/a'$. Hence by definition

$$\eta_n = k_n b_\infty$$

and

$$\langle \eta \rangle = \sum_{n=1}^{\nu} k_n \eta_n \Big/ \sum_{n=1}^{\nu} k_n = (b_\infty \pi / 3a')(2\nu + 1), \tag{3}$$

where ν is the highest occupied quantum number. Then

$$\langle \eta \rangle \approx \frac{\pi}{4}\left(1 + \frac{\pi}{2k_F a'}\right), \tag{4}$$

which is the result given by Appelbaum and Blount.[6] In the following it is shown that k_F for the quantized system is the same as for the bulk case to order $(1/k_F a)^2$ and similarly for the chemical potential. The fact that the chemical potential does not change, even though the box is expanded, is a rather surprising consequence of the sum rule when applied to this quantized case.

The number of electrons per unit area of the bulk material normalized to geometric film thickness a is given by $k_{F0}^3 a/3\pi^2$.

The sum over allowed wave vectors [see Fig. 1(b)] now gives the number of electrons per unit area in the quantized physical film and is given as

$$\frac{1}{2\pi}\sum_{n=1}^{\nu}(k_F^2 - k_n^2). \tag{5}$$

Conservation of charge requires that

$$\frac{k_{F0}^3 a}{3\pi^2} = \frac{1}{2\pi}\sum_{n=1}^{\nu}(k_F^2 - k_n^2) = \frac{1}{2\pi}\left(\nu k_F^2 - \frac{\pi^2}{a'^2}\frac{\nu}{6}(2\nu^2 + 3\nu + 1)\right), \tag{6}$$

which implies that

$$k_F \cong k_{F0}\left(1 + \frac{\pi^2}{12 k_{F0}^2 a'^2}\right). \tag{7}$$

For usual metals, $b_\infty \approx k_F^{-1} \approx 1$ Å. Our model is consistent to high accuracy with the sum rule and constancy of k_F for films over 5 Å. That k_F is constant to order of $(1/k_F a)^2$ is crucial to the arguments that follow and provide results that are completely different from previous ones.

For a spherical Fermi surface, the constancy of k_F implies the constancy of the chemical potential μ. To demonstrate the physical origin of this constancy, one can use the Thompson and Blatt (TB)[2] expression for μ normalized to a larger box. Their expression is

$$\mu = \frac{\pi a \hbar^2}{\nu m}\left(\frac{N}{V} + \frac{\pi}{6a^3}\nu(\nu + \tfrac{1}{2})(\nu + 1)\right). \tag{8}$$

It should be noted that in this expression the first term is a consequence of the electron density and the second term involves the quantization condition. This second term causes a dramatic increase in μ with decreasing thickness a. In our case we let a' replace a, and $\nu = a' k_F/\pi$ (at thicknesses where shape resonances occur) with k_F, the bulk value as shown previously,

$$\mu = \frac{\pi a' \hbar^2}{\nu m}\left(\frac{Na}{V_0 a'} + \frac{\pi}{6a'^3}\nu(\nu + \tfrac{1}{2})(\nu + 1)\right). \tag{9}$$

The "physical" volume V is now a'/a times the geometric volume V_0. Making appropriate expansions and keeping terms to order $1/k_F a$ we obtain

$$\mu \cong \frac{\pi^2 \hbar^2}{k_F m}\left[\frac{N}{V_0}\left(1 - \frac{6\pi}{8k_F a}\right) + \frac{k_F^3}{6\pi^2}\left(1 + \frac{3\pi}{2k_F a}\right)\right]$$

with

$$N/V_0 = k_F^3/3\pi^2, \tag{10}$$

$$\mu \cong \hbar^2 k_F^2/2m. \tag{11}$$

It should be noted that the decrease in density because of the extended "box" is compensated to first order by the increase due to the quantization conditions.

CALCULATION OF THE ENERGY GAP

Our procedure is essentially to follow the TB calculation but using a larger box that takes into account the leakage of the electrons beyond the geometric surface as shown in Fig. 1. Essentially, the charge leaks out beyond the ion cores an inverse Fermi wave vector, as one might expect from Thomas-Fermi screening arguments. Besides doing the calculation in a larger box, it is also assumed that in the region beyond the ion cores the electron-phonon interaction falls off rapidly (in the spirit of taking $1/k_F$ to be the decay length of the interaction).

Following TB we assume a δ-function potential of the form

$$v(\vec{r}_i - \vec{r}_j) = -J\delta(\vec{r}_i - \vec{r}_j) \tag{12}$$

and where J is the interaction constant. Using

periodic boundary conditions in the y and z directions with periodicity distance L,

$$\langle k,-k|v|k',-k'\rangle=\frac{-J}{L^2}\int_0^a[u_n(x)u_{n'}(x)]^2dx \qquad (13)$$

if

$$|\epsilon_k-\mu| \text{ and } |\epsilon_{k'}-\mu|<\hbar\omega_D,$$

where

$$u_n(x)=\left(\frac{2}{a'}\right)^{1/2}\sin\frac{n\pi(x+b_\infty)}{a'} \qquad (14)$$

and ω_D is the Debye frequency. Expression (13) assumes that the interaction from $-b_\infty$ to 0 and from a to a' (see Fig. 1) is reduced owing to the electron gas extending beyond the ion cores, as mentioned previously. Note that now the wave function is periodic in a' whereas in the original calculation the distance was the film thickness a. The overlap integral which in the original work was

$$\int_0^a[u_n(x)u_{n'}(x)]^2dx=\frac{1}{a}\left(1+\frac{\delta_{nn'}}{2}\right) \qquad (15)$$

now becomes

$$\begin{aligned}\int_0^a[u_n(x)u_{n'}(x)]^2dx&=\int_{-b_\infty}^{a'}[u_n(x)u_{n'}(x)]^2dx\\&\quad-2\int_a^{a'}[u_n(x)u_{n'}(x)]^2dx\\&\cong\frac{1}{a'}\left(1+\frac{\delta_{nn'}}{2}\right)-\frac{2Bb_\infty}{a'}\ .\end{aligned} \qquad (16)$$

The constant B is of order unity, and we shall use $b\equiv 2Bb_\infty$. We have approximated the integral in the above form since the normalization over a' makes the integral from zero to the geometrical thickness a function of n and n' and the gap equation for the energy gap function Δ_n cannot be solved analytically. In the above form we write

$$\Delta_n=K^{-1}\sum_{n'}\Delta_{n'}A_{n'}\int_0^a[u_n(x)u_{n'}(x)]^2dx, \qquad (17)$$

where

$$A_n=\sinh^{-1}(\hbar\omega_D/\Delta_n), \qquad (18)$$

and $K=2\pi\hbar^2/mJ$, following Thompson and Blatt. Using Eq. (16),

$$\Delta_n\left(1-\frac{A_n}{2Ka'}\right)=\frac{1}{Ka'}\left(1-\frac{b}{a'}\right)\sum_{n'=1}^{\nu}\Delta_{n'}A_{n'}. \qquad (19)$$

In this form Δ_n and A_n are independent of n. Hence

$$1-\frac{A_n}{2Ka'}=\frac{1}{Ka'}\left(1-\frac{b}{a'}\right)\nu A_n\Delta_n. \qquad (20)$$

Using the definition of A_n

$$\begin{aligned}\Delta_n&=\hbar\omega_D(\sinh A_n)^{-1}\\&\cong 2\hbar\omega_D\exp-\left(\frac{Ka'}{\nu(1-b/a')+\frac{1}{2}}\right).\end{aligned} \qquad (21)$$

Note that for large a'

$$\nu=k_Fa'/\pi \qquad (22)$$

and writing

$$K=k_F/\pi\rho,$$

then

$$\Delta_n\cong 2\hbar\omega\exp\left(-\frac{1}{\rho(1-Bb_\infty/a')}\right). \qquad (23)$$

T_c is given by the usual BCS relation between gap and transition temperature.

COMPARISON OF RESULTS WITH TB

The present result differs from the TB result in several important ways.

(i) In the TB calculation k_F and μ vary with thickness. In the present calculation k_F is essentially constant and μ is also constant with thickness.

(ii) In the TB calculation the envelope for the peaks at shape resonances

$$T_{cp}=1.14\Theta_D\exp\left(-\frac{a_\nu K}{\nu+\frac{1}{2}}\right), \qquad (24)$$

where a_ν is given by

$$a_\nu^3=(\pi V/2N)[\nu^3-\tfrac{1}{3}\nu(\nu+\tfrac{1}{2})(\nu+1)] \qquad (25)$$

and Θ_D is the Debye temperature. The valley envelope is

$$T_{cv}=1.14\Theta_D\exp\left(-\frac{a_\nu K}{\nu-\frac{1}{2}}\right) \qquad (26)$$

and the intermediate value defined by letting ν change by $\frac{1}{2}$ is

$$T_{ci}=1.14\Theta_D\exp(-a_\nu K/\nu). \qquad (27)$$

Note these curves give an "average" rise in T_c as thickness decreases.

In the present calculation, for the purposes of comparison we unrealistically let $b=0$, now the envelope curves become

$$\begin{aligned}T_{cp}&=1.14\Theta_D\exp\left(-\frac{Ka'}{k_Fa'/\pi+\frac{1}{2}}\right),\\T_{cv}&=1.14\Theta_D\exp\left(-\frac{Ka'}{k_Fa'/\pi-\frac{1}{2}}\right),\\T_{ci}&=1.14\Theta_D\exp\left(-\frac{Ka'}{k_Fa'/\pi}\right)\\&=1.14\Theta_D\exp(-1/\rho)\\&=T_{c\ \text{bulk}}.\end{aligned} \qquad (28)$$

Owing to the constancy of k_F, T_{ci} is now the bulk T_c. Hence even in this case there is no increase in the average T_c. This is because in TB, μ increases with decreasing thickness and in our calculation μ is constant with thickness. This accounts for the major difference between these calculations besides the consideration of loss in electron-phonon interaction at the boundaries, which is discussed below.

(iii) Because of the spread of the electrons past the ion cores the result for T_c in the present case actually contains a further difference from TB. The envelope curves are given by

$$T_{cp} = 1.14\Theta_D \exp\left(-\frac{Ka'}{(k_F/\pi)a'(1-b/a')+\frac{1}{2}}\right),$$

$$T_{cv} = 1.14\Theta_D \exp\left(-\frac{Ka'}{[(k_F/\pi)a'-1](1-b/a')+\frac{1}{2}}\right), \quad (29)$$

$$T_{ci} = 1.14\Theta_D \exp\left(-\frac{Ka'}{[(k_F/\pi)a'-\frac{1}{2}](1-b/a')+\frac{1}{2}}\right).$$

In Fig. 2(b) we show the various envelope curves for $b = 1$ Å, which is a physically reasonable case. In this case it can be seen that the average T_c decreases as thickness is reduced.

DISCUSSION

There are two aspects to the present calculation; one is the effect of the thinness of the films on the usual electronics parameters such as k_F and μ, and the other is the effect on the superconducting transition. It is interesting that the self-consistent extension of the geometric boundary as given by Sugiyama[7] leads to the constancy of k_F and μ even in the quantized case. It appears that the theory of the transport properties in Bi thin films should be looked at again in this regard. Turning to superconductivity the constancy of k_F and μ eliminates any quantum enhancement of T_c. Furthermore, consideration of the overlap integral in the extended "box" actually causes T_c to go down.

If we examine the equation for the reduction of T_c in the case where b/a is small, it can be put in the form for the decrease in T_c owing to the proximity effect in the Cooper limit.[8] In this Cooper-limit case $T_c \sim \langle\omega\rangle e^{-1/\rho}$, where ρ is given by

$$\rho_{\text{eff}} = \frac{N_n^2 V_n d_n + N_s^2 V_s a}{N_n d_n + N_s a}, \quad (30)$$

where N, V, d are the density of states, the net electron-phonon interaction, and the thicknesses of the respective normal (n) and superconducting (s) films. If we take N_n and d_n as the density of states in the fall-off region outside the ion cores[9] and take $V_n = 0$, then

$$\rho_{\text{eff}} = N_s V_s \left(\frac{N_s a}{N_s a + N_n d_n}\right)$$

and

$$T_c \sim \langle\omega\rangle \exp[(-1/N_s V_s)(1 + N_n d_n/N_s a)]$$

or

$$T_c = T_{c0} \exp(-N_n d_n / N_s^2 V_s a). \quad (31)$$

If we identify $N_n d_n/N_s$ with b and $N_s V_s$ is taken to be ρ, then Eq. (31) is very similar to Eq. (23). Now the factor $1 + b/a$ is in the numerator, which is the expansion $1/(1 - b/a')$ for small b/a'. Note also that the thickness appearing is a, whereas a' in-

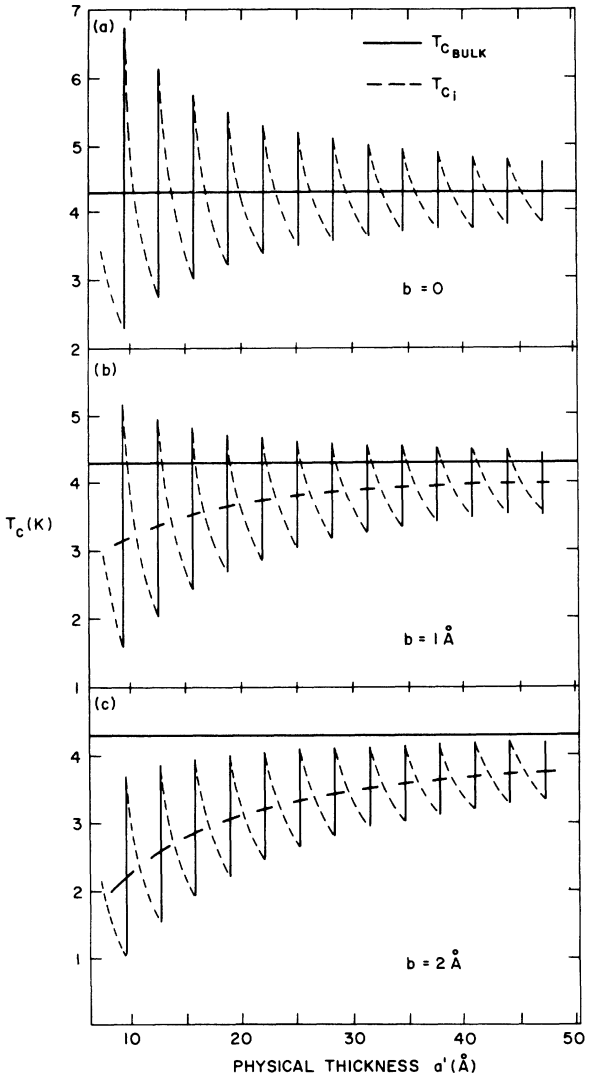


FIG. 2. This set of curves shows the variation of T_c with physical thickness a' at various values of b. Here for convenience, we take $K = k_F = 1$ Å^{-1} and $1.14\Theta_D = 100$. T_c takes a jump at shape resonances. The peak, valley, and intermediate T_c values are given by Eq. (29).

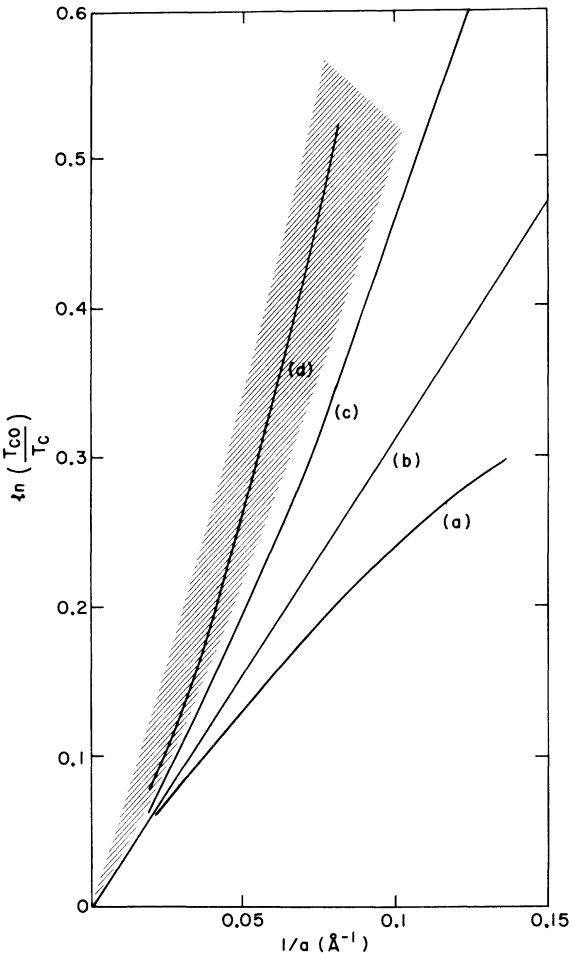


FIG. 3. Graph shows the comparison of our calculations for T_{ci} with experimental results. All curves are theoretical curves with $b = 1$. Granular correction parameter $c = 0$, 10, 20 for curves a, c, d, respectively. Curve b shows the Cooper limit. The experimental results in Ref. 10 lie in the shaded area.

cludes the electron-tail region.

Finally Eq. (31) can be put in the form $\ln(T_{c0}/T_c) = b/\rho a$. Curve b in Fig. 3 shows this linear dependence with $1/a$. Thus the surface with its reduced electron density tends to depress T_c for the adjoining bulk. However, we mention that for films of the order of 10 Å these results [Eq. (29), Fig. 3, curve a] show a smaller depression than for the Cooper limit. In Fig. 3 we show the asymptotic agreement, and the deviation at the smallest thickness. This deviation is due to the quantized nature of the present calculation.

As far as numerical analysis of various data goes, it appears that the present calculation with $b = 1$ provides a change in T_c of the order of a couple of K in Pb at 10 Å which does not quite describe the larger depression in T_c observed experimentally. In films with high resistance per square $R_\square$ fluctuations can depress T_c of the order of 1 K in 10 Å films[10] and activated conduction can also be expected to lower T_c of the order of 1 K.[10] It is possible that the present model can be modified to provide a greater lowering of T_c for the thinnest films in the following way. In the thinnest films one might expect the film to break up as evidenced by the large increase in $R_\square$ and hence a shorter mean free path. If we now assume a first-order correction for the further loss of electron-phonon interaction due to film breakup, then we write

$$b \approx b_0 + c/a,$$

then

$$b/a \approx b_0/a + c/a^2.$$

It can be seen that the c/a^2 term provides an additional factor to the previous result. In Fig. 3 we plot $\ln(T_{c0}/T)$ against a^{-1} for $b_0 = 1$ Å and different values of c. It can be seen that this expansion can be used to phenomenologically account for the film breaking up with additional loss of electrons and decreases of T_c in the very thinnest films. The connection to $R_\square$ is clear if we take a approximately equal to the mean free path l, then

$$b/a \sim b_0/a + c/al \sim b_0/a + c'R_\square.$$

Of course, this analysis is just meant to sketch how better quantitative agreement can be obtained with actual data. Clearly, the actual structure and model to describe real films is not known at this time and further analysis is unwarranted. However, in general, the present calculation from first principles does suggest that a decrease of T_c, not very different from that observed, can be expected.

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