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Proximity effects and the generalized Ginzburg-Landau equation*

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A computer program has been developed which finds solutions of the generalized Ginzburg-Landau equation subject to de Gennes's boundary conditions. The resulting information on the spatially varying order parameter is then interpreted *vis-à-vis* experimental data on both superconductor–insulator–normal-metal–superconductor Josephson tunneling systems, and ultrasonic-surface-wave attenuation.

I. INTRODUCTION

It is well known that when a superconductor and a normal metal are placed in intimate contact with one another induced superconductivity will arise in the normal metal as a result of the leakage of Cooper pairs into it. Similarly, a system consisting of two superconductors is expected to exhibit a transition temperature somewhat above the lower of the constituent T_c's.[1]

Over the past years a variety of theories and experiments have been devised to reveal and clarify this proximity effect. Theoretically the approaches have centered on the Gor'kov formulation[2] of the microscopic theory, usually in the dirty limit. For example, de Gennes[3] was able to treat the case of a dirty superconductor–normal-metal (S-N) with the additional proviso that T be in the neighborhood of the system transition temperature. He derived boundary conditions governing the order parameter at free and metallic surfaces and then proceeded to determine the behavior of certain limiting systems (e.g., thick films). Other attempts to find solutions of the Gor'kov self-consistency equation for the gap parameter have been made by Werthamer,[4] Silvert and Cooper,[5] and Yeh.[6] The generalized Ginzburg-Landau equation derived by Gor'kov[2] was later employed by Fulde and Moorman in treating the thermodynamic properties (principally specific heat) of proximity systems.[7] Just recently the same equation was applied to a calculation of thermal conductivities; in this work by Migliori and Ginsberg[8] good agreement was obtained between theory and experiment for indium-thallium structures. Other current interest in the problem is reflected by the experiments of Deutscher *et al.*[9] on the thermal conductivity of silver-lead bismuth specimens.

We have elected to apply the generalized Ginzburg-Landau theory to two situations. In the first, the attenuation of ultrasonic surface waves in the normal layer of an S-N system is interpreted as a probe of the total number of Cooper pairs which have leaked into the normal film. In the second, the maximum Josephson tunneling current for multiple-layer superconductor–insulation–normal-metal–superconductor (SINS) structures is monitored as a function of temperature; such results are known to reflect the amplitude of the order parameter—and thus its temperature dependence—at the oxide–normal-metal interface.

II. GENERALIZED GINZBURG-LANDAU EQUATIONS IN S-N SYSTEMS

The problem of describing the behavior of S-N layers is reduced to solving[8]

$$\left(\ln\frac{T}{T_c}-\frac{\pi^2}{4}\bar{\xi}^2\frac{d^2}{dx^2}\right)\Delta(x)+\frac{7}{8}\frac{\zeta(3)}{(\pi k_B T)^2}\Delta^3(x)=0, \tag{1}$$

where $\Delta(x)$ is the (real) gap parameter, T_c is the transition temperature of the given material or isolated thin film, $\bar{\xi}^2=\frac{1}{3}\xi l$, l is the electron mean free path (in all equations to follow, l will be understood to mean the mean free path in a sample of thickness d; corrections for finite d may be achieved by means of Fuchs's[10] theory), $\xi=\hbar v_f/2\pi k_B T$, v_f is the Fermi velocity, T is the ambient temperature, $\zeta(q)$ is the Riemann ζ function, and $\hbar$ and k_B have their usual meanings. This equation is valid providing the following conditions prevail: $H=0$, $T\sim T_c$, $l/\xi<1$ (dirty limit), $\Delta(x)$ slowly varying. Equation (1) must be applied to the S and N regions separately with the further stipulation that solutions satisfy the following boundary conditions of de Gennes[3]: $d\Delta/dx=0$ at a free surface and Δ/NV and $(D/V)d\Delta/dx$ both continuous across a metallic interface. $D=\frac{1}{3}v_f l$ is the diffusion coefficient and N and V are the density of electron states at the Fermi surface and the electron-electron coupling constant, respectively.

We shall prefer to deal with the conventional Ginzburg-Landau order parameter ψ, which in the dirty limit is related to the gap parameter Δ via

$$\psi = (n\pi l/4k_B T_c \hbar v_f)^{1/2}\,\Delta, \tag{2}$$

where n is the density of electrons. Equation (1) thus becomes

$$\frac{d^2\psi}{dx^2} - \left(\frac{24k_BT}{\pi l\hbar v_f}\ln\frac{T}{T_c}\right)\psi - \left(\frac{84\zeta(3)T_c}{n\pi^4 l^2 T}\right)|\psi|^2\psi = 0. \tag{3}$$

It is apparent that in a bulk superconducting sample a uniform solution exists for (3) in the form

$$\psi_0^2 = \left(\frac{2n_s\pi^3 l_s k_B T^2}{7\zeta(3)\hbar v_{fs} T_{cs}}\right)\ln\frac{T_{cs}}{T}. \tag{4}$$

We shall find it convenient to scale *all* of the order parameters by this common factor. We thus write $\psi = \psi_0 f$ and note that, consequently, $0 \le f^2 \le 1$ on the S side of a proximity sandwich, although no such restriction applies to the N region.

Consequently,

$$\frac{d^2 f}{dx^2} + \alpha^2(f - f^3) = 0 \qquad \text{in S}, \tag{5a}$$

$$\frac{d^2 f}{dx^2} - \alpha^2(\beta^2 f + \delta^2 f^3) = 0 \qquad \text{in N}, \tag{5b}$$

where

$$\alpha^2 = \left(\frac{24k_BT}{\pi l_s\hbar v_{fs}}\right)\ln\frac{T_{cs}}{T}, \tag{6a}$$

$$\beta^2 = \frac{l_s v_{fs}\ln(T/T_{cn})}{l_n v_{fn}\ln(T_{cs}/T)}, \tag{6b}$$

$$\delta^2 = \frac{n_s T_{cn}}{n_n T_{cs}}\left(\frac{l_s}{l_n}\right)^2. \tag{6c}$$

Subscripts s denote parameters of the S layer, while subscripts n denote parameters associated with the N region. Note that a finite T_{cn} is assumed, and thus $N_nV_n > 0$. de Gennes's boundary conditions[3] become

$$\left(\frac{T_cv_f}{nl}\right)^{1/2}\left(\ln\frac{1.14\Theta_D}{T_c}\right)f \qquad \text{continuous}, \tag{7a}$$

$$\left(\frac{T_cv_f}{nl}\right)^{1/2} Nlv_f\left(\ln\frac{1.14\Theta_D}{T_c}\right)\frac{df}{dx} \ \text{continuous}. \tag{7b}$$

Θ_D is the appropriate Debye temperature. At a free surface $df/dx = 0$.

Solutions of Eqs. (5a) and (5b) may be written as

$$f_s^2(x) = \frac{f_{0s}^2(2-f_{0s}^2)\,cn^2(u,k)}{2(1-f_{0s}^2)+f_{0s}^2 cn^2(u,k)}\ , \tag{8}$$

where $cn(u,k)$ is the Jacobi elliptic cosine[11] with arguments

$$u = (2-f_{0s}^2)(d_s - x)\,\alpha/\sqrt{2}, \tag{9a}$$

$$k^2 = f_{0s}^2/(2-f_{0s}^2), \tag{9b}$$

$$f_n^2(x) = f_{0n}^2/cn^2(u,k), \tag{10}$$

where

$$u = (f_{0n}^2 + \beta^2/\delta^2)\,\alpha\,\delta\,\sqrt{2}\,(x+d_n), \tag{11a}$$

$$k^2 = \frac{f_{0n}^2 + 2\beta^2/\delta^2}{2(f_{0n}^2+\beta^2/\delta^2)}. \tag{11b}$$

d_s and d_n are the thicknesses of the superconducting and normal layers, respectively. We have selected a coordinate system whose origin is at the S-N interface and for which S lies in the region $d_s \ge x \ge 0$ and N lies in $-d_n \le x \le 0$. The physical meaning of the parameters f_{0s}^2, f_{0n}^2 is now clear; they are the relative order-parameter amplitudes at the free surfaces. They must be selected in such a way as to guarantee the boundary conditions (7a) and (7b) at $x = 0$.

This task of finding suitable values for f_{0n}^2, f_{0s}^2 is a formidable one. It required a computer-search technique which involved partitioning a candidate plane and looking for grid squares through which the two curves defined implicity by (7a) and (7b) simultaneously passed. As in all such procedures, a tradeoff must be established between desired numerical accuracy and computational time and cost. The output from our program basically consists of tolerance limits on the parameter pair within which the true values are known to lie. Therefore these numerical uncertainties must be properly accounted for in any calculations which employ f_{0n}^2 and f_{0s}^2 as inputs. The error bars which appear in Figs. 1 and 4 reflect this situation.

III. ULTRASONIC SURFACE-WAVE ATTENUATION

The attenuation of ultrasonic surface waves was studied by Kratzig,[12] whose experiments were performed on Cu/Pb, Ag/Pb, and Al/Pb double layers. A bias magnetic field was used to "switch off" the proximity-induced superconductivity in the N region, thereby breaking all the Cooper pairs which had leaked across the interface. The extra attenuation which resulted was interpreted as being necessarily proportional to the product of the electron mean free path and the total number of Cooper pairs which had been present in the N layer at the given temperature. From such data experimental values of the ratio A_d/A_∞ were deduced, where A_d is the total number of Cooper pairs for film thickness d and A_∞ is the corresponding (finite) value for $d \to \infty$.

Theoretically, A_d should be proportional to the integral of the order parameter squared throughout N. In his analysis Kratzig employed the hyperbolic functions obtained by de Gennes[3] in his thick-film "one-frequency" approximation of the Gor'kov[2] condition. Satisfactory agreement was apparently achieved between experiment and theory in the test case Al/Pb, for which the NV values were known; the method was then employed to infer NV products for copper and silver from the corresponding experimental data.

We have used our computer procedure to solve the generalized Ginzburg-Landau Equations (5a) and (5b)

TABLE I. Experimental data for proximity sandwiches.

	Ultrasonic attenuation		Tunneling	
Material	Al[N]	Pb[S]	Zn[N]	Sn[S]
T_c (°K)	1.189	7.21	0.91	3.73
v_f (cm/sec)	1.29×10^{8}	0.5×10^{8}	0.87×10^{8}	0.54×10^{8}
Θ_D (°K)	420	96	308	189
n (cm^{-3})	1.81×10^{23}	0.33×10^{23}	0.491×10^{23}	0.588×10^{23}
d (Å)	variable	2500	see Fig. 4	2400
l (Å)	800	1000	see Fig. 4	see Fig. 4
N_n/N_s	0.463		0.471	

with the numerical values of various physical constants given in Table I (which are appropriate to Kratzig's Al/Pb sample). The value of f_{0n}^2 was sought for a variety of normal layer thicknesses extending to $d_n = 7500$ Å. For each thickness, f_{0n}^2 was then employed in (10) and $f_n^2(x)$ was numerically integrated over the normal region. Values of the integral become fairly constant for $d_n > 3500$ Å; thus the ratio

$$\frac{A_d}{A_\infty} = \frac{\int_0^{d_n} f_n^2(x)dx}{\int_0^\infty f_n^2(x)dx} \tag{12}$$

could be ascertained quite accurately. The results are plotted in Figs. 1(a) and 1(b) for two different temperatures. Also plotted are the corresponding results for the de Gennes thick-film solutions, [3] which have been selected to conform to Kratzig's analysis.

$$f_n(x) \propto \frac{\cosh[K(x+d_n)]}{\cosh(Kd_n)}, \tag{13}$$

where

$$K^2 = \left(\frac{6\pi k_B T}{\hbar v_f l}\right)\left(1 - \frac{2(NV)}{1 - C(NV)}\right), \tag{14}$$

$$C \equiv \ln(1.14\Theta_D/T) - 2.$$

K is just the reciprocal of the depth of penetration of the pairs on the N side.

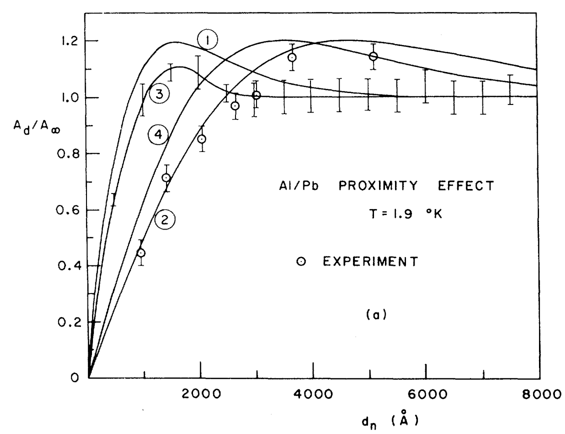
A more correct expression involving K is given by[3]

$$\ln(T_{cn}/T) = \psi(\tfrac{1}{2} - \tfrac{1}{2}\xi^2K^2) - \psi(\tfrac{1}{2}). \tag{15}$$

When Kratzig's analysis is repeated using this relation for K, curve 4 of Fig. 1(a) is obtained. Our numerical solution appears to favor the thick-film approximation assuming $NV = 0$, and the "correction" to the one-frequency theory for finite NV seems to be excessive. It appears that the cubic term partly cancels the effect in the linear theory of having a finite interaction in the normal metal. As expected, all results converge in the limit $d_n \to \infty$. It does appear, however, that there is significant conflict for finite d_n *and* NV. We note the apparently stronger agreement *experimentally* (the experimental points were obtained from Ref. 12) with curve 2 in Fig. 1(a). However, the correction to K for finite NV is quite sensitive to temperature [note Fig. 1(b)], and it would be interesting to see if experimental evidence would favor such rapid changes. It is also revealing to note the partial insensitivity of A_d/A_∞ to the exact functional form of $f_n^2(x)$, i.e., whether hyperbolic or Jacobi elliptic functions are employed.

IV. JOSEPHSON TUNNELING IN SINS SYSTEMS

An approximate treatment of SIS junctions by de Gennes[13] revealed that the amplitude of the anticipated dc Josephson current was proportional to the product of the order parameters immediately on either side of the insulating barrier. This conclusion suggests the use of an SINS Josephson tunnel structure to probe the amplitude of the order parameter at the insulator–normal-metal interface; such an experiment ought to be a useful tool in gauging the decay of the order parameter within the normal layer. Greenspoon and Smith[14] and



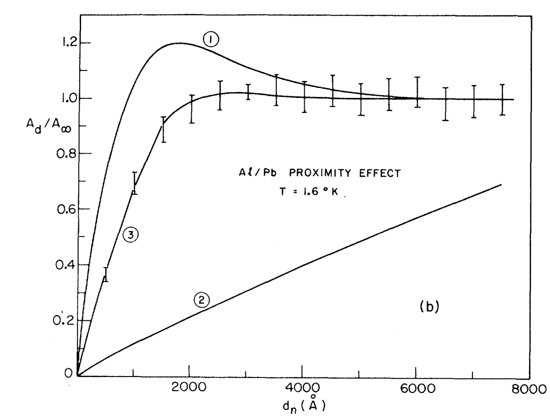


FIG. 1. Plots of the relative number of Cooper pairs, A_d/A_∞, as a function of normal layer thickness for the cases (i) one-frequency approximation with $NV = 0$; (ii) one-frequency approximation with $NV = 0.175$; (iii) generalized Ginzburg-Landau theory, and (iv) one-frequency approximation with $NV = 0.175$ and more accurate form for K.

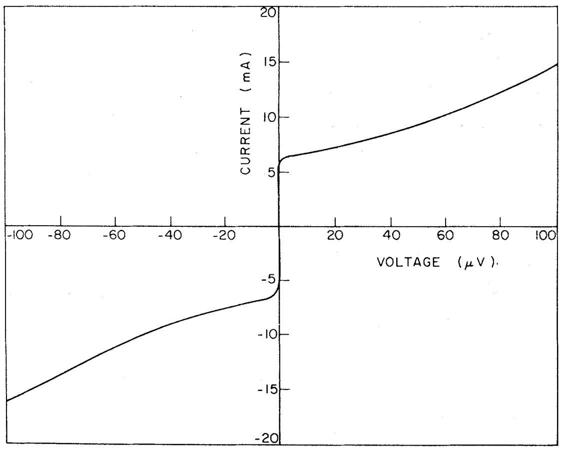


FIG. 2. Current-voltage characteristic of the Josephson subsystem in a thin-film Sn-SnO-Zn-Sn sandwich.

more recently Romagnan *et al.*[15] analyzed such experiments and obtained apparently satisfactory agreement with the observed behavior of I_{max} versus T. However, rather simple functional forms were assumed for $f_n^2(x)$ and $f_s^2(x)$.

We have performed new experiments and calculations designed to test the theoretical model in a more definitive manner.

Evaporated thin-film junctions of the form Sn-SnO-Zn-Sn were studied in which the tin-oxide layer formed the weak-coupling barrier through which Josephson tunneling took place. The Zn-Sn layers constituted the proximity-effect sandwich; zinc and tin were chosen because they have small mutual solubility and do not form intermetallic compounds. The metal films were evaporated onto glass slides at room temperature and at a pressure of about 2×10^{-6} Torr. The first tin layer was deposited on the glass substrate and then oxidized in dry air at 600 Torr for 8 h. Film thicknesses were measured with a Hilger Watts N130/D187 interferometer.

Voltage and current contacts were provided at the two tin layers. The current leads were connected to a 100-Hz ac constant-current source, and a flicker-free current-voltage characteristic for the Josephson subsystem was then displayed on a Tektronix 5030 oscilloscope operating in the X-Y mode. An electronic cursor could be positioned along the scope Y axis and a readout from its bias circuit enabled the maximum zero-voltage Josephson current to be logged as a function of temperature.[16] A typical current-voltage characteristic is shown in Fig. 2. The junctions exhibited a Fraunhofer-type variation of I_{max} with applied magnetic field; we therefore conclude that Josephson tunneling was taking place and that microshorts were not present to any measurable degree. A calibrated germanium thermometer was employed in the I_{max}-vs-T measurements.

During the junction fabrication a strip of zinc was evaporated on the same glass slide. Its resistance was monitored, using a four-terminal network, at 77 and 4.2 °K. The electronic mean free path l_n was then estimated using a technique due to Toxen *et al.*[17] The resulting values are given in the data box in Fig. 4. The coherence lengths were estimated from $\xi = (\hbar v_f l / 6\pi k_B T)^{1/2}$, which for $T \sim 3$ °K and $l \sim 1000$ Å gives $\xi \sim 1000$ Å. The dirty-limit condition is clearly not well satisfied in either tin or zinc films, since in both cases we anticipate mean free paths of order 1000 Å.

Theoretical fits were obtained in the following manner. The material constants appropriate to the thin-film structures (see Table I) were made available to the computer program which then evaluated f_{0n}^2, f_{0s}^2 for the N-S substructure. A polynomial approximation for $\Delta(T)$ was employed to obtain the associated value of the order parameter ψ_{BCS} in the isolated superconductor. Figure 3 is presented as an example of the type of spatial variation encountered for $f^2(x)$. The product $G(T) = \psi_{BCS} f_{0n} \psi_0$ is then supposedly proportional to $I_{max}(T)$. In our experiments the mean free path for the superconducting film was not known, and this then became the single adjustable fitting parameter[18] with the following exception: All $G(T)$-vs-T curves are scaled in such a way that they pass through the experimental curve at $T = 2.0$ °K. Although this is a somewhat *ad hoc* procedure, it does give sets of curves which are easy to assess. We should bear in mind that the theory does not provide us with an absolute scale—only the relative temperature dependence is important.

A typical experimental curve is presented in Fig. 4 together with representative theoretical data. It is readily apparent that it is not possible to achieve really good agreement by adjusting l_s. We are thus

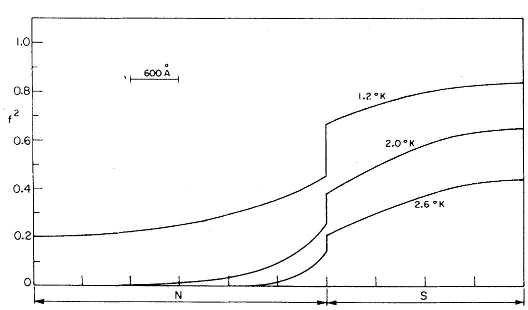


FIG. 3. Example of the variation of the relative amplitude of the Ginzburg-Landau order parameter obtained by the computer program. These characteristics are for the conditions $l_s = 2000$ Å, $l_n = 1130$ Å, $d_n = 3600$ Å in Sn/Zn layers.

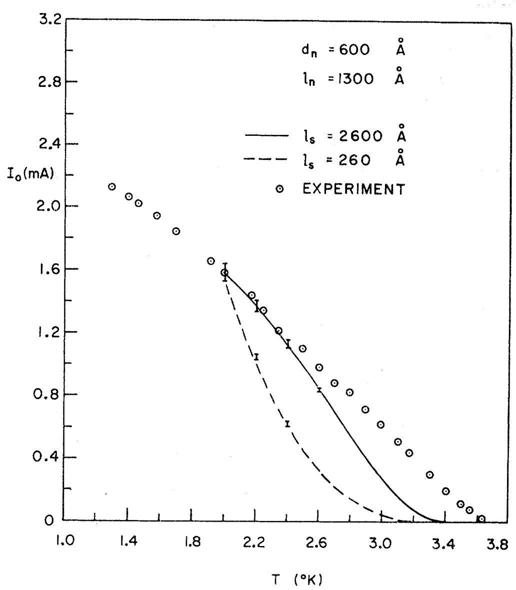


FIG. 4. Maximum tunneling current for SINS structure as a function of temperature and theoretical $G(T)$ curves for two extreme choices of the superconducting mean free path, 260 and 2600 Å.

led to question the apparently excellent agreement found by others.[14,15] In the first place, these previous endeavors employed crude approximations of $\psi_n(x)$; yet it is quite possible that the functional role of the fitting parameters (extrapolation lengths, for example) permitted better over-all results than might have been expected. Secondly, somewhat restricted ranges of temperature were investigated, and we might well anticipate an apparent improvement in the present results if a narrower thermal window were adopted. Again, previous optimism in interpreting results was perhaps premature. There is also the question as to how exactly proportional $I_{\max}$ is to $\psi_{\mathrm{BCS}}\,\psi_n$. Such a conclusion flows only from specific assumptions concerning the barrier and the boundary conditions applicable there. We ought to keep in mind, too, the necessity in the de Gennes theory[3,13] of being in the vicinity of the transition temperature of the layered system. Finally, the dirty-limit condition is known to be not well satisfied in these experiments. Work is in progress to make tunneling measurements on S-N sandwiches where both layers are well into the dirty regime.

V. DISCUSSION AND CONCLUSIONS

Three experimental probes of the proximity effect are thermal conductivity, ultrasonic attenuation, and tunneling. In each case previous publications have indicated significant agreement with Werthamer[4]- and de Gennes[3]-type solutions for the order parameter. However, we note:

(i) The thermal-conductivity results of Migliori and Ginsberg (see Fig. 5, Ref. 8) show that even an extremely crude approximation for $\Delta(x)$ such as a linear function gives surprisingly adequate agreement with experiment.

(ii) As we have demonstrated, the integrations involved in calculating the total number of Cooper pairs give similar results whether hyperbolic or elliptic functions are used.

(iii) Careful comparison of experiment and theory in the tunneling system reveals a less than satisfying agreement. This may, however, merely reflect the fact that the experimental conditions deviated somewhat from some of the requirements of the theory.

Thus we conclude that the first two techniques, because they involve integrals of the order parameter, are partially insensitive to the precise shape of $f_n(x)$ and so cannot be relied upon to clearly differentiate between competing theories of the proximity effect. The results quoted, while suggestive, are not definitive.

The tunneling method would seem to be preferable, but clearly greater attention must be paid to such conditions as $l/\xi \ll 1$.

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