Decay of Persistent Currents in Small Superconductors*

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The thermodynamic fluctuations of the order parameter in a superconductor are shown to be able to cause the decay of a "persistent" current in a ring-shaped conductor. Calculations have been made of the lifetimes of these currents, which indicate that in very thin wires this decay should be detectable. We also show that a true phase transition, distinguished by an infinitely sharp change of resistivity, is possible only in an infinite three-dimensional specimen. In one- and two-dimensional samples, on the other hand, no *infinitely* sharp change of resistivity occurs but, instead, the resistance drops smoothly and rapidly towards zero as $T \rightarrow 0°K$.

ONE of the outstanding problems of superconductivity is that of explaining the lifetime of persistent currents in ring specimens. In this paper we will show that it is possible to set an upper limit on this lifetime by considering the effects of thermodynamic fluctuations in the specimen. These fluctuations provide a means by which the persistent current can decay. Decay by this means should be observable in small specimens where the thermodynamic fluctuations can be appreciable. In large specimens, on the other hand, the lifetimes are predicted to be enormously large, in agreement with the experimental evidence.

This work was motivated by the consideration of Ferrell[1] and Rice[2] of the role played by the dimensionality of the specimen on the existence of superconductivity or off-diagonal–long-range order[3] (ODLRO). They have shown that in one-dimensional specimens, in particular, fluctuations in the density or of the superconducting order parameter make it impossible for ODLRO to occur in these specimens. One might then be led to conclude that superconductivity would be impossible in a one-dimensional sample, that is, one in which the transverse dimensions are small compared to the length. In particular, one might conclude that superconductivity would be impossible in a linear macromolecule of the type discussed earlier by the author.[4] This does not necessarily follow, for we do not know at present whether ODLRO is a sufficient *and necessary* condition for the existence of superconductivity. In order to investigate whether superconductivity can be ruled out in these systems, we have extended the arguments of Ferrell and Rice and used them to determine directly a limit on the lifetime of a "persistent" current in finite ring-shaped superconducting samples. We obtain the result that for a system in which the range of the interaction force is finite, a phase transition defined by an infinitely sharp change of conductivity can occur only in a sample which is infinite in at least three dimensions. We are particularly interested in samples which are infinite in only one of the three dimensions. In these, the average electrical resistivity at finite temperatures never drops to a value which is absolutely zero. However, in most cases, for temperatures appreciably less than the bulk T_c, the resistance drops to an exceedingly small fraction of the normal resistance. We find then that while we have neither a true phase transition nor the existence of ODLRO because of the fluctuations in a one-dimensional system, we can still have a state of greatly enhanced conductivity at low temperatures. We must stress, however, that in our argument we follow Ferrell and Rice in assuming the existence of an order parameter locally. There is some reason to believe that for specimens so narrow that the lateral dimensions are less than the Fermi wavelength, it may be impossible for an order parameter to occur here at all.[5] This is a different problem from that of the fluctuations and we make no attempt to examine this here, except to discuss what bearing our results will have on this problem. Also, in our arguments we have confined ourselves to the problem of thermodynamic fluctuations alone: i.e., fluctuations in which a small part of the specimen deviates, for example, in its temperature or density from that of the rest of the specimen, but within each small part equilibrium at this different temperature or density is maintained at all times. We have not considered fluctuations to states which are not describable by such local values of the intensive parameters. Because of this, our results give only an upper limit on the lifetime of the persistent current. It is for this reason that an experimental investigation of these lifetimes would be particularly valuable, for it would show how important these microscopic fluctuations were in determining the properties of the superconducting state.

THERMODYNAMIC FLUCTUATIONS

It has been shown by Gor'kov[6] that the Ginzburg-Landau theory[7] of superconductivity is equivalent to

* Work supported by the U. S. Office of Naval Research.
[1] R. A. Ferrell, Phys. Rev. Letters **13**, 330 (1964).
[2] T. M. Rice, Phys. Rev. **140**, A1889 (1965).
[3] C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).
[4] W. A. Little, Phys. Rev. **134**, A1416 (1964).
[5] S. Engelsberg and B. B. Varga, Phys. Rev. **136**, A1582 (1964); D. C. Mattis and E. H. Lieb, J. Math. Phys. **6**, 304 (1965).
[6] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959)].
[7] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

the BCS[8] theory, at least in the vicinity of the transition temperature. These Ginzburg-Landau equations provide a simple means for incorporating spatial and time varying fluctuations in the condensate which would be cumbersome in the more microscopic forms of the BCS theory. Recently it has been shown by Werthamer and Tewordt[9] that the Ginzburg-Landau theory has a wider range of validity for materials with a short mean free path. Furthermore, there is an impressive amount of experimental evidence to show that it gives an excellent account, both qualitatively and quantitatively, of the known phenomena of superconductivity.[10,11] In this paper we shall be concerned primarily with superconductivity in specimens with at least one dimension extremely small. In this domain, the Ginzburg-Landau equations have been particularly successful in explaining old phenomena and predicting new.[12,13] For the above reasons, we believe that these equations form a valid basis for our arguments except, perhaps, for samples so small that the lateral dimensions are small compared to the Fermi wavelength. The resultant lamination of the Fermi sphere introduces special considerations which in this case may prevent the existence of an order parameter.

For our arguments, the existence of an order parameter plays an essential role. However, Ferrell in his paper[1] has argued that the Gor'kov function $F(x)$, which is related to the Ginzburg-Landau order parameter, vanishes in a one-dimensional system. This aspect of his argument is not correct. The error lies in his incorrect replacement of the definite integral in his equation (3) by the indefinite integral. The definite integral has as its limits the phase of the order parameter at points x and x', respectively. This phase difference is, in principle, subject to measurement. The use of the indefinite integral, however, replaces the appropriate phase difference with the absolute value of the phase. This is tantamount to measuring the phase at x with respect to some arbitrary external standard, and this is not subject to physical measurement. Ferrell's conclusion, however, that ODLRO should not occur in one dimension survives, nevertheless, because $G(x,x')$, which occurs in the criterion for ODLRO, involves the phase difference between x and x' rather than any absolute phase.

It appears, then, that one is on safe ground in assuming the existence of an order parameter at least locally subject to the above restrictions and that the free energy depends upon it through the Ginzburg-Landau equations. We wish to show, then, first that the thermodynamic fluctuations which have been shown by Rice to be capable of destroying ODLRO in a one-dimensional system will not destroy flux quantization or a persistent current in a closed loop, unless a fluctuation occurs which is of such an amplitude that the order parameter is driven to zero for some section of the loop.

Consider the Ginzburg-Landau equations:

$$F(\psi)=\int[a|\psi(r)|^2+b|\psi(r)|^4+c|\nabla\psi(r)|^2]d^3r, \quad (1)$$

where the order parameter $\psi(r)$ is a complex function with real amplitude $\Delta(r)$ and phase $\phi(r)$, and where

$$\psi(r)=\Delta(r)\exp i\phi(r). \quad (2)$$

In the usual treatment, one ignores fluctuations and determines the equilibrium value of $\psi(r)$ by minimizing (1) with respect to $\Delta(r)$ and $\phi(r)$. However, other functional forms of $\Delta(r)$ and $\phi(r)$ are possible and will occur with a probability $e^{-\beta F(\psi)}$, where $F(\psi)$ is the computed value of the free energy in (1) for the given functional forms of $\Delta(r)$ and $\phi(r)$. The actual order parameter will fluctuate among these possibilities. Rice took these into account for a one-dimensional system and showed that the appropriately weighted average of the function $\langle\langle\psi(r)\psi^*(r')\rangle\rangle$ over all possible forms of the order parameter was such that

$$\lim_{|r-r'|\to\infty}\langle\langle\psi(r)\psi^*(r')\rangle\rangle\to 0. \quad (3)$$

This is the condition for the absence of ODLRO in the system,[3] and consequently we see that ODLRO cannot exist in such a one-dimensional system. Let us extend this argument by considering a sample in the form of a wire of diameter d and length l joined back on itself to form a closed loop. We will consider initially the case where $d<\xi_l$, so that variations of $\psi(r)$ across the wire can be neglected so that we may use the one-dimensional form of the Ginzburg-Landau equations. Later we will discuss the limitation of this approach. Byers and Yang[14] have shown that if the free energy of such a loop varies with the magnetic flux Φ through it, then persistent currents will flow and it will exhibit the phenomenon of flux quantization. Consequently, we ask whether or not the free energy of the loop as given by (1) varies with the magnetic flux through it.

For such a loop geometry, the boundary condition on $\psi(r)$ is that it should be single valued. This, therefore, imposes upon the phase the condition that

$$\phi(l+r)-\phi(r)=2\pi n, \quad (4)$$

where n is an integer. Because of this, each possible form of the order parameter $\psi(r)$ can be classified according to the integer describing the phase change

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[9] N. R. Werthamer, Phys. Rev. **132**, 663 (1963); L. Tewordt, *ibid.* **137**, A1745 (1965).
[10] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].
[11] T. G. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).
[12] M. Tinkham, Phys. Rev. **129**, 2413 (1963).
[13] L. Meyers and W. A. Little, Phys. Rev. Letters **13**, 325 (1964).
[14] N. Byers and C. N. Yang, Phys. Rev. Letters **7**, 46 (1961). See also Ref. 4 above.

round the loop in Eq. (4). Let us consider that we group these ψ's in subensembles of given n.

We must include the contribution of the vector potential $\mathbf{A}(r)$ into the Ginzburg-Landau equations in order to take the contribution of the flux into account. As indicated above, we will take initially the one-dimensional form of these equations:

$$F(\psi)=\int\psi^*(x)\left\{a+b|\psi(x)|^2+c\left[i\frac{\partial}{\partial x}-\mathbf{A}(x)\right]^2\right\}\times\psi(x)dx. \quad (5)$$

For any arbitrary form for the order parameter belonging to a given subensemble n, we find that

$$F(\psi_n)=a\int\Delta^2(x)dx+b\int\Delta^4(x)dx+\frac{4\pi^2c(n+\alpha)^2}{I}+\int\beta^2(x)\Delta^2(x)dx, \quad (6)$$

where $I=\int_0^l[dx/\Delta^2(x)]$, $\beta(x)$ is a real function independent of the flux but dependent upon $\psi_n(x)$, and α is $\Phi/(hc/2e)$. We see then that for all order parameters which lie in a given subensemble, the free energy will depend upon the flux unless the integral I is infinite. For a finite ring this integral can be infinite only if $|\Delta(x)|$ is zero in at least one place. As a result of this, the expectation value of the free energy over the subensemble of states of given n, $\langle\langle F(\psi_n)\rangle\rangle$, must vary with the flux. It is convenient to think of a single system moving in time through the various possible phase points representing the various fluctuations, rather than an ensemble of the systems with a given number in each particular region of phase space. In this view, then, we see that so long as the system fluctuates among the states of just this subensemble the free energy will be flux-dependent, and consequently during this period a persistent current will not decay. It will fluctuate in magnitude depending upon the instantaneous value of I, but its fluctuations will be centered on a value determined by n. Likewise, the trapped flux will fluctuate about a value n times the appropriate flux quantum, and flux quantization will be maintained.

In order to understand the decay of a persistent current, then, we must determine how the system can make a fluctuation from one subensemble n to another n'. We will argue that this is only possible if a fluctuation occurs which drives the order parameter $|\Delta(x)|$ to zero at least at one point in the loop.

FLUCTUATIONS BETWEEN SUBENSEMBLES

We recall that the order parameter $\psi(x)$ describes the behavior of a large number of particles. Changes in this order parameter can occur, for example, because of an influx of heat to the region near x or of an influx

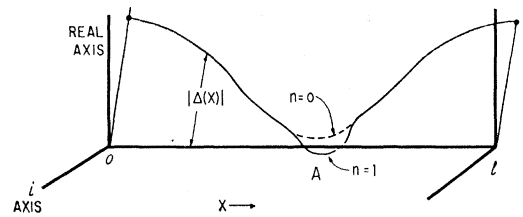

FIG. 1. The order parameter $\psi(x)$ which is complex is drawn as a function of position. Two possible configurations are shown, one for an order parameter in the subensemble $n=0$ and the other for $n=1$. Near A, $\psi_1(x)$ makes an excursion round the Argand diagram while $\psi_0(x)$ does not.

or efflux of particles to or from this region. It seems reasonable to assume that changes in $\psi(x)$ must occur continuously because it involves many particles. Each particle, on the average, must gain a little energy for the over-all energy to increase. It is unreasonable to expect the large number of particles described by the order parameter to gain an increment of energy discontinuously. However, we could expect them to gain energy continuously, and thus the total energy density would change continuously through all neighboring values of the energy density. We would expect, for the same reason, that changes in the density and in the entropy density would also occur continuously. On the basis of this argument, we contend that all fluctuations occur such that the order parameter changes continuously or, in other words, through configurations which lie infinitely close to one another. On this assumption we can determine how a fluctuation can carry the system from one subensemble, n, to another, n'.

Consider the illustration (Fig. 1). This depicts the variation of the amplitude $\Delta(x)$ and phase $\phi(x)$ for two possible configurations of the order parameter, $\psi_0(x)$ and $\psi_1(x)$, lying in the subensembles $n=0$ and $n=1$, respectively. The total change of phase from x to $x+l$ for ψ_0 is zero, while for ψ_1 it is 2π. We have taken the flux Φ to be zero. We have chosen the amplitude and phase of the two configurations to be identical except in the region near A. In this region, $\psi_1(x)$ makes an excursion round the Argand diagram to rejoin $\psi_0(x)$ a little beyond A, while $\psi_0(x)$ makes no such excursion. In this region, $\psi_0(x)$ and $\psi_1(x)$ have the same amplitude but, of course, differ in phase. It is clear from this figure that it is only possible for $\psi_0(x)$ and $\psi_1(x)$ to lie infinitely close to one another everywhere if they both drop to zero at the same point. At this point $\psi_1(x)$'s excursion round the Argand diagram could coincide with $\psi_0(x)$ if both had zero amplitude. Our assumption that fluctuations progress only through configurations which lie infinitely close to one another then leads us to the conclusion that a fluctuation from one subensemble n to another n' can occur only if $|\Delta(x)|$ fluctuates to zero at some point in the loop. Our picture of the decay of a "persistent" current then proceeds as follows: Let us suppose that at $t=0$ the order parameter of the loop lies in a subensemble n.

Now fluctuations will occur among the states of this subensemble as discussed earlier. Eventually a fluctuation will occur with such an amplitude that $\Delta(x)$ is driven to zero in some part of the loop. The system may then proceed into any other subensemble n'. It will then fluctuate in this new subensemble until again $\Delta(x)$ is driven to zero, at which time it may progress to some other subensemble. On the average, it will gradually find its way to that value of n' which minimizes the free energy and will then fluctuate in and around this neighborhood. Within each subensemble, the system behaves like an ordinary superconductor exhibiting flux quantization and a "persistent" current which fluctuates about a mean value. Where $\Delta(x)$ fluctuates to zero, this part of the loop reverts temporarily to the normal state exhibiting its normal electrical resistance. For the rest of the time the loop exhibits zero resistance. We can therefore calculate the time average of the resistance of the loop by determining what fraction of the time some part of the loop is normal and thus has its normal resistance.

We proceed to calculate this in the following way. First, we note that the order parameter $\psi(x)$ in some small part of the loop may be considered to be a function of the local value of the density (of electrons) ρ and of the local temperature T. Fluctuations in either T or ρ can cause the order parameter to drop to zero in some regions of the loop. For small fluctuations, standard fluctuation theory[15] shows us that the probability of a fluctuation occurring of amplitude ΔT or ΔV, where ΔV is the change of volume V containing N particles, is

$$\omega=\exp\left\{-\left(\frac{C_v}{2kT_0^2}\right)(\Delta T)^2+\frac{1}{2kT_0}\left(\frac{\partial p}{\partial V}\right)_{T,N}(\Delta V)^2\right\}. \quad (7)$$

Here C_v is the heat capacity of the small volume which fluctuates in temperature by ΔT. For a given mean temperature T_0, we can readily calculate the probability that a fluctuation can occur such that ΔT is sufficient to raise a small part of the body above the temperature T_c at which the order parameter goes to zero. This is the meaning of T_c for our further calculations. For fluctuations in density or ΔV, we can obtain some idea of the magnitude ΔV must reach for the order parameter to go to zero. This we can do by assuming that the BCS approximate expression,

$$kT_c=1.14\hbar\omega\exp[-1/N(0)V] \quad (8)$$

is valid in this small part of the body. Here $N(0)$ and V depend upon the density, and thus density fluctuations at a given temperature T_0 can cause T_c to fall below T_0. An increase of electron density will increase $N(0)$ but decrease V because of increased screening. Thus we can get an upper bound on the variation of T_c with density by assuming that V does not change with density. A simple analysis for a free-electron gas and the use of (8) shows that the rms fluctuation of the temperature in (7) is greater than the rms fluctuations of T_c due to density fluctuations by a factor of the order of $\epsilon_f/16kT_c$. Taking the Coulomb repulsion into account gives a factor which is even larger than this; consequently, it is an excellent approximation to ignore the fluctuations of the density and consider only fluctuations in the temperature.

We have to consider fluctuations which are not small, in which case Eq. (7) is an inadequate approximation. In this case let us imagine that the filament of superconductor is immersed in an environment at some mean temperature T_0 as illustrated in Fig. 2. This seems to be the most realistic situation of experimental interest. Quite generally,[15] then, the probability ω of some small part of the filament fluctuating to some temperature T is

$$\omega=\exp\left\{-\frac{u(T)-u(T_0)-T_0[s(T)-s(T_0)]}{kT_0}\Omega\right\}, \quad (9)$$

where $u(T)$ is the internal energy per unit volume of the filament at temperature T and $s(T)$ is the corresponding entropy. Ω is the volume of the small part of the filament.

The order parameter cannot change very rapidly in a distance much smaller than the mean-free-path reduced coherence length ξ_l without raising the free energy appreciably; consequently, the smallest volume whose temperature fluctuations we need consider is a volume having the diameter of the filament and a length ξ_l.

The *time average* of the resistance of any part of the filament is then

$$R=R_n\left[\int_{T_c}^{\infty}dT\exp\left\{-\frac{u(T)-u(T_0)-T_0[s(T)-s(T_0)]}{kT_0}\Omega\right\}\Bigg/\int_0^{\infty}dT\exp\left\{-\frac{u(T)-u(T_0)-T_0[s(T)-s(T_0)]}{kT_0}\Omega\right\}\right]. \quad (10)$$

[15] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958).

In the numerator, the integral should run from 0 to ∞; however, for $T<T_c$, $R=0$, so this part makes no contribution. For $T>T_c$ we assume that $R=R_n$ and thus can be factored from the integral, and we get the expression above.

We can get a good idea of the variation of R with T by considering samples such that the small volume which can fluctuate in T is large enough so that $u(T)$ and $s(T)$ for this volume can be approximated to the values of the bulk material. In this case, for T less than T_c we know empirically that $u(T)$ and $s(T)$ are given approximately by[16]

$$u_s(T)=(3\gamma/4T_c^2)(T^4-T_c^4)$$

and

$$s_s(T)=T^3/T_c^2. \tag{11}$$

Here γT is the electronic specific heat per unit volume for the normal state.

For $T>T_c$ we have

$$u_n(T)=\tfrac{1}{2}\gamma(T^2-T_c^2),\qquad s_n(T)=\gamma T. \tag{12}$$

The general behavior of the variation of the resistance with temperature is illustrated in Fig. 3. The width of the transition (from $0.9R_n$ to $0.1R_n$) is of the order of $2(2kT_c/\Omega\gamma)^{1/2}$, i.e., twice the root-mean-square (rms) fluctuations of the local temperature. It is clear from this that unless the volume Ω which undergoes the temperature fluctuations is infinite, the resistance will not drop discontinuously to zero at T_c. Thus for a finite coherence length ξ_l and $d<\xi_l$ a discontinuous change in resistance cannot occur at T_c.

For finite samples we have evaluated the expression (10) approximately, using (11) and (12). In the denominator, the approximate expression (7) has been used in evaluating the integral because the major contribution to this integral comes from small fluctuations for which (7) is valid. In the numerator we have dropped terms of order g^2 and higher, where $g=\{kT_0/\gamma\Omega(T_c-T_0)^2\}^{1/2}$, and consequently our expression is not valid for T_0 very close to T_c. The behavior here is continuous, however, and one could, with some labor, obtain the exact details if they were needed. The results we obtain for $T_0<T_c$ and $T_0>T_c$ are, respectively,

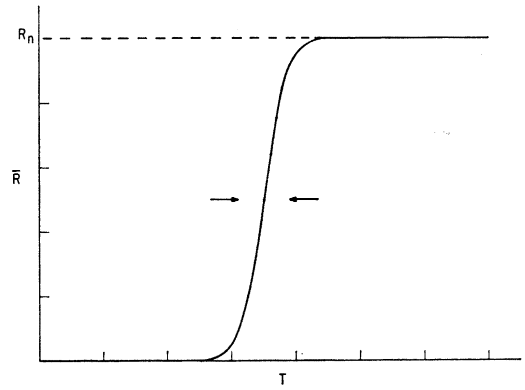

FIG. 3. General form of the mean resistance of a finite superconducting sample as a function of the temperature. The width indicated by the arrows is approximately $2(2kT_c/\Omega\gamma)^{1/2}$.

$$R=R_n\left\{\exp\left[-\frac{[f_n(T_0)-f_s(T_0)]\Omega}{kT_0}\right]\right\}\left(\frac{\gamma T_0\Omega}{\pi kT_c^2}\right)\times\left(\frac{kT_0}{\pi\Omega(T_c-T_0)}\right)\exp\left[-\frac{\gamma\Omega}{2kT_0}(T_c-T_0)^2\right], \tag{13}$$

where $f_n(T_0)$ is the free energy per unit volume of the normal state, $f_s(T_0)$ is the corresponding free energy for the superconducting state, and

$$R=R_n\left\{1-\frac{2kT_0}{\pi(T_0-T_c)^2\Omega\gamma}\exp\left[-\frac{\gamma\Omega}{2kT_0}(T_0-T_c)^2\right]\right\} \tag{14}$$

for $T_0>T_c$.

These can be represented by a single parameter $S\equiv\gamma\Omega T_c/k$, and the reduced temperature $t=T_0/T_c$. For $T<T_c$, we show the behavior in Fig. 4.

From the above we see that in spite of the absence of ODLRO in such a one-dimensional system, a significant reduction in the normal resistance will occur for temperatures appreciably below the bulk T_c value.

One can appreciate better the rapid change of resistance with temperature by considering the decay time for a current in a wire in the form of a circle of diameter 1 cm and wire thickness d. In Table I we give the lifetime computed from the ratio of L/R as a function of temperature for two wire diameters, 100 and 360 Å ($S\approx 20$ and 1000, respectively). Here we assume $\xi_l\approx d$ and $T_c=3.7$°K.

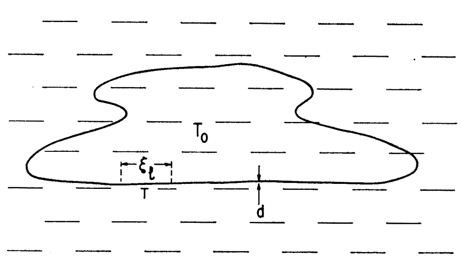

FIG. 2. Illustration of a long thin superconductor of diameter d connected in the form of a closed loop and immersed in a bath at a temperature T_0. Fluctuations of the local temperature T of a small section of length $\approx\xi_l$ can occur and lead to decay of a "persistent" current.

[16] See for example, M. Tinkham, in *Low Temperature Physics*, edited by C. DeWitt, B. Dreyfus, and P. G. de Gennes (Gordon and Breach Science Publishers, Inc., New York, 1962), p. 151.

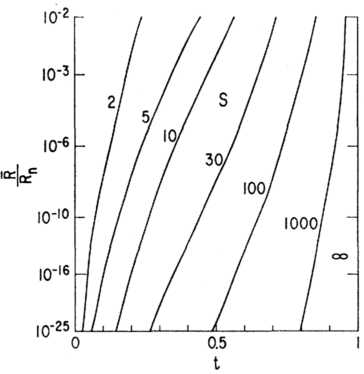

FIG. 4. Plot of the average resistance of a thin superconducting wire as a function of reduced temperature $t=T/T_c$ and parameter $S\equiv\gamma\Omega T_c/k$, where Ω is of the order of $(\pi d^2/4)\xi_l$ and d is the wire diameter.

For wires of diameters appreciably larger than this, it is clear that the transition from the relaxation time characteristic of the normal state to that of an immeasurably long relaxation time would occur in a minute temperature interval and normally would be masked by small differences of the transition temperature due to impurities and strains. Only in samples with dimensions comparable to those discussed above would it be possible to observe directly the decay of the persistent current due to the thermodynamic fluctuations. Measurements on samples of this size would be particularly valuable in determining the role other nonthermodynamic fluctuations play in determining the decay lifetime.

TABLE I. Computed lifetimes for two Sn wires, one of 100 Å diameter and the other of 360 Å.

Lifetime	100 Å wire (°K)	360 Å wire (°K)
$\approx 10^{-14}$ sec	3.7	3.7
10^{-7} sec	2.0	3.4
10^{-4} sec	1.5	3.26
1 sec	1.25	3.10
10 days	1.0	3.06
10^6 years	0.75	2.90

DISCUSSION

By considering just the thermodynamic fluctuation of the temperature of a thin superconducting specimen, we have shown that the lifetime for the decay of a persistent current is not infinite. However, for wires larger than a few hundred angstroms in diameter the lifetime for the decay attains an immeasurably large value within a small fraction of a degree below the bulk transition temperature.

The extension of these ideas to samples of macroscopic size in the second and third dimensions is not trivial. In the first place, the classification of the order parameters into subensembles of definite n, strictly speaking, fails for any finite width of the sample. For, in principle, a variation of $\psi(r)$ across the sample can make the phase change of the order parameter along a path on one side of the sample differ from that along the other, so that a vortex line is enclosed by the specimen. For the case we have considered, however, where $d<\xi_l$, the free energy for such a vortex configuration is so high away from the immediate neighborhood T_c that the system spends a sufficiently small time in it that our classification according to a definite n is a workable approximation. For samples in which one of the transverse dimensions is greater than ξ_l, we must include the possibility of the existence of such vortex configurations and the interactions these would have with an external field and a conduction current. If the magnetic field is large enough, then an equilibrium array of these vortices can exist and one obtains the Abrikosov state characteristic of the type-II superconductor.

It is worthwhile noting that the decay mechanism we have considered amounts to the entry of one flux unit (*not* $hc/2e$, but this value corrected to the dimensions of the sample[17]) in the average flux during a transition between subensembles. This is superficially similar to the mechanism which generates the flux flow resistance of type-II superconductors. The dissipative mechanism, i.e., the movement of flux through the specimen, is the same in both cases; however, the important difference lies in the role played by the magnetic field. In the type-II superconductor, a magnetic field greater than H_{c1} is necessary in order to maintain the sample in the Abrikosov state with an *equilibrium* distribution of vortices throughout the sample. The movement of this array due to the Lorentz force interaction with the conduction current gives rise to the dissipation of the current. The magnitude of this dissipation is determined by the strength of the pinning sites of the vortex array. This problem has been treated by several authors.[18] The situation which we have examined is that were the magnetic field is so small, $H\ll H_{c1}$, that there is, firstly, no equilibrium vortex array and, secondly, the magnetic field interactions, can be neglected. In this case, it is not the strength of the pinning sites of the vortices which determines the dissipation but rather the probability for the creation of a vortex. In the very thin sample we have considered, i.e., $d<\xi_l$, the existence of a vortex in the wire would require a higher free energy than that which is necessary to drive the order parameter to zero across a section of the wire. For this reason the preferred decay mechanism is by the latter means. For samples with transverse dimensions comparable to the penetration depth or larger, the free energy required for the creation of a vortex will be lower than that needed to drive the order parameter to zero across a section of the wire. In

[17] J. Bardeen, Phys. Rev. Letters **7**, 162 (1961).
[18] See for example, P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. **36**, 39 (1964).

this case the current can still decay but the mechanism is more closely akin to the flux flow resistance found for type-II superconductors.

In a Josephson junction the penetration depth is anomalously large and the order parameter anomalously small; consequently, the most probable way for flux to cross the junction, assuming that the junction is short compared to the penetration depth, is by a fluctuation in which the order parameter fluctuates to zero as discussed here rather than by the migration of a flux line across the junction as in a type-II superconductor.

It is useful to note that in the absence of an external magnetic field the energy per unit length of a vortex is of the order of $\Phi_0^2/4\pi^2\lambda^2$, with approximately equal contributions coming from the field energy and from the current. Here $\Phi_0=hc/2e$, and λ is the penetration depth. Even for quite thin films at temperatures a little below T_c this energy is appreciably larger than kT_c so that the equilibrium density of these thermally excited vortices will be extremely small. For example, consider a film of Sn, 100 Å thick, the mean free path, $l\approx 100$ Å, $\xi_0=10^4$ Å, $\lambda_L(0)\approx 500$ Å at $t=T/T_c=0.99$. We have[19] $\lambda\approx 0.62\lambda_L(0)[\xi_0/l(1-t)]^{1/2}$, giving $\lambda\approx 3.1\times 10^4$ Å. The total energy of this vortex line is therefore of the order of $18kT_c$, and the probability of finding a vortex in this region at this temperature is $\approx e^{-18}$. We observe, however, that for any finite film thickness the energy of such vortices, while large, cannot be infinite, so that near enough to T_c an appreciable density of these will occur. Similarly, the pinning energy cannot be infinite for a finite film. The resistive transition to the superconducting state must therefore be continuous because of the gradual decrease in the number of these vortices per unit area as the temperature is lowered below T_c. As the film thickness is made larger, the total energy of a vortex line through the film increases, and consequently we should expect a sharper transition to the superconducting state to occur. Only for an *infinite three*-dimensional sample can one expect a discontinuous transition. Such a discontinuity is characteristic of a phase transition. One may conjecture then that no true phase transition should occur in either the one- or two-dimensional cases.

In the presence of a magnetic field, the problem becomes considerably more complicated in detail, although it is easy to see that such a field lowers the energy of those vortices with the appropriate orientation with respect to the field until at H_{c1} an equilibrium array becomes possible. Below H_{c1}, the number of thermally excited vortices will then be field-dependent and likewise the resistance.

One can also apply these considerations to the hypothetical superconducting macromolecule suggested earlier.[4] If an order parameter can exist in such a linear molecule and we accept the estimates[4] of $T_c\approx 2000$°K, a coherence length of 30 Å, and the density of states at the Fermi surface used in that calculation, we obtain a value of $S\approx 2.5$. (In this system where the lateral degrees of freedom of the electrons are frozen out, we calculate the electronic specific heat of the molecule per unit length, and Ω is replaced by the coherence length ξ_l.) Referring to Fig. 4, we see that below room temperature ($t<0.15$) the average resistance will have fallen to a very small fraction of its normal resistance. A much more rapid drop in resistance with temperature can be gotten by cross-linking the individual polymer filaments so that they form a three-dimensional net. By so doing one raises the energy required for a flux line to penetrate through the mass of filaments. Also, if the polymer filament is imbedded in some other material or fluid instead of vacuum, the fluctuations of the temperature of the filament will be tied to the fluctuations of some part of its immediate environment. This will effectively increase the volume which can undergo the thermal fluctuations and again increase the effective value of S.

We see then that the thermodynamic fluctuations are not sufficient in themselves to rule out the possibility of a state of greatly enhanced conductivity occurring at the low temperatures in a linear macromolecule. This point can only be settled by examining whether or not an order parameter can exist locally in such a system. In this regard we may note that the exactly soluble one-dimensional model of Mattis and Lieb[5] shows no evidence of the superconducting state for any form of the interaction potentials. This must not be construed as evidence that such an order parameter cannot exist here, for we have shown that in any one-dimensional system such as that of Mattis and Lieb, an order parameter, if it exists, must fluctuate so that it moves through all the different subensembles n discussed earlier. The exact solution to the thermodynamic properties of this system, therefore, must be an average over all these subensembles of different n. It is not difficult to see from Eq. (6) that such an average washes out all the flux dependence in the free energy and thus yields a state which in equilibrium has no superconducting properties. The true equilibrium state in this case is not superconducting but, as we have seen in our examples above, the approach to equilibrium can be so slow at low temperatures that a *nonequilibrium state* can persist for a sufficient length of time to give a greatly enhanced conductivity.

CONCLUSION

We have shown that the fluctuations of both the amplitude and the phase of the Ginzburg-Landau order parameter do not destroy a persistent current in a "one-dimensional" superconducting loop unless a fluctuation occurs which drives the amplitude of the order parameter to zero at all points on a surface which severs

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the loop. We calculate the probability of this occurring by using standard fluctuation theory. From this we are able to calculate the time-average resistance of the samples, and we find that while no infinitely sharp change of resistance occurs at any temperature, nevertheless, the resistance falls significantly below the normal resistance of the specimen as the temperature is lowered appreciably below the bulk T_c. A true phase transition to the superconducting state appears to be possible only in an infinite three-dimensional sample. In one dimension, if the range of the interaction force is finite, no phase transition is possible. The resistance of the one-dimensional system does approach zero, however, as $T \rightarrow 0°K$.

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Studies of Surface Transport Currents in Type-II Superconductors; a Surface-Flux-Pinning Model

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The critical surface transport current of type-II films is measured as a function of magnetic field ($H_{c1} < H < H_{c3}$), of the angle that the magnetic field makes with the surfaces, of surface condition, and of film thickness. The results show that the critical surface current (1) is much smaller than that predicted by the Abrikosov-Park model, (2) does not vary systematically with film thickness as predicted by certain recent theories, (3) *increases* as the surface is roughened, (4) decreases sharply as the perpendicular component of the applied magnetic field is increased, and (5) increases sharply as the applied magnetic field is lowered through H_{c2}. These results are interpreted as evidence for surface flux pinning, i.e. of a surface-critical-state model, rather than as evidence for any of the published theoretical models. In our model, quantized flux threads or spots intercepting the surface of the sample are pinned at surface pinning sites. When a transport current is applied, a Lorentz force is exerted on these surface flux threads or spots. At a transport current level below the intrinsic theoretical limit, the Lorentz force exceeds the pinning force; flux moves across the surface, a steady voltage is detected, and a critical surface current is thereby defined.

A. INTRODUCTION

THE large transport supercurrents supported in the mixed state ($H_{c1} < H < H_{c2}$) in hard superconductors like Nb_3Sn and Nb-Zr alloys flow predominantly through the bulk of the conductor.[1] These supercurrents exist by virtue of the interaction between the quantized magnetic flux threads that permeate the superconductor and some appropriate defect structure such as grain boundaries,[2] precipitate particles,[3] radiation damage,[4] etc.,—an interaction that inhibits the motion of the flux threads and the appearance of a voltage. It has recently been shown that the surfaces of a type-II superconductor can also support a transport supercurrent.[5–8] This effect has been demonstrated in at least two types of experiments. In the first type it has been shown that shielding surface transport supercurrents can be induced by a changing external magnetic field.[5,6] In the second type, that which we[7] and Bellau[8] perform, the ability of the surface to carry a transport supercurrent is demonstrated by applying transport currents directly to films and prisms. In both types of experiments it is found that a surface transport supercurrent will flow both in the mixed state and in the region of the Saint James and de Gennes surface film ($H_{c2} < H < H_{c3}$).[9] A

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