First order phase transitions in Ferromagnet/Superconductor layered structures

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We study the thermodynamics of clean structures composed of superconductor (S) and ferromagnet (F) layers and consisting of one or more SFS junctions. We use fully self consistent numerical methods to compute the condensation free energies of the possible order parameter configurations as a function of temperature $T$. As $T$ varies, we find that there are phase transitions between states characterized by different junction configurations (denoted as “0” or “π” according to the phase difference of the order parameter in consecutive S layers). We show that these transitions are of first order. We calculate the associated latent heats and find them to be measurable.

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A plethora of new ideas and devices has been emerging from the study of nanostructures as they pertain to the field of spintronics. An important part of this development has occurred through the study of the rich and varied phenomena that occur in heterostructures involving superconductors (S) and ferromagnets (F).

The physics of such F/S heterostructures is dominated by the proximity effects that arise from the competition between superconducting and magnetic orderings in the materials comprising the structure, with each of the corresponding order parameters penetrating into the other material. These effects follow from normal and Andreev reflection processes at the interfaces. In the latter process, an electron encounters one of the interfaces, is converted into a hole with opposite spin and traverses in the opposite direction. For S/N interfaces (where N is a non-magnetic, non-superconducting metal) the dynamics of charge transport is degenerate with respect to the electron spin quantum variable. This is not true, however, in the case we consider here, where superconducting regions are separated by magnetic interlayers.

In SFS trilayers, as well as in multilayers built from a sequence of such structures (SFSFS…), the spin-splitting effect of the magnet produces important and nontrivial changes in Andreev and other scattering processes. The exchange field in the ferromagnet breaks the time-reversal symmetry and generates a superconducting state where the Cooper pairs acquire a finite momentum resulting in a spatial modulation of the superconducting pair amplitude in the F region. Depending on the geometric and material characteristics of the SFS trilayer, its thermodynamic equilibrium state can be a “0” or a “π” state, depending on the value of the phase difference between the superconducting order parameters in the two S electrodes. It is this twofold possibility that lies at the foundation of the many spin-based switching phenomena, which in turn are the basis for devices, including superconducting π qubits and memory elements. For larger SFSFS…S type heterostructures the order parameter may or may not flip between any pair of consecutive S layers, leading to a variety of possible configurations, which can be characterized as a sequence of 0 and π junctions.

Continual advances in nanoprocessing methods have made it possible to fabricate high quality structures containing SFS junctions, which have encouraged further study of these systems. From the thermodynamics point of view, a 0 to π transition as the temperature was varied was inferred from Josephson current measurements in Nb/CuNi/Nb junctions. The Josephson coupling in similar structures was also found to cross over from positive to negative, depending on the F layer thickness, indicating again a 0 to π switch. Under many experimental conditions, a change in the second-order Josephson coupling component was associated with the 0 – π crossover while for other conditions, the nonlinear current-phase relation did not reveal any change in the second-order Josephson coupling.

The thermodynamics of F/S structures has been directly examined largely in terms of studying the transition temperature to the normal state. A first order phase transition to the normal state has been predicted in spin-valve ferromagnet-superconductor-ferromagnet (FSF) nanostructures with parallel magnetization alignments in thin F layers. For antiparallel orientation of the magnetization, the transition was found to be always second order. The application of a bias voltage up to a critical value can cause the phase transition to be first order for both P and AP alignments of the magnetization. For F/S bilayers with stripe domain structures, superconductivity appears via a first order transition. In some cases, with the action of an applied field, the compensating screening currents can enhance the superconducting state. The theoretical literature that examines the thermodynamic transitions between 0 and π configurations in SFS type structures is more sparse. It has been argued that the transition that takes place in Josephson junctions is continu-
ous when the F layer thickness is uniform but it rounds off when it is variable. To further understand the underlying competition between the various possible states and to better tailor these structures for practical applications, it is imperative to clarify the thermodynamics of systems potentially containing $\pi$ junctions by investigating the parameters that may influence a first or second order phase transition from a $0$ state to a $\pi$ state or vice versa.

The objective of this paper is to clarify some of these issues by rigorously considering the thermodynamics of clean layered systems consisting of one or more SFS junctions so as to identify and characterize any phase transitions involving $0 - \pi$ flipping. It has been shown at low-temperature that for given S and F widths, exchange energy and other material parameters, multiple spatial configurations of the self consistent pair amplitude can exist as local minima of the energy. The larger the number of layers, the more combinations were found to be possible. Among the various solutions, the ground state was found from accurate condensation energy computations. Here on the other hand, we have the more ambitious objective of studying the possible competing states as a function of temperature $T$ through a careful analysis of the free energy differences. We find that, as $T$ varies, phase transitions associated with flipping of SFS junctions from a $0$ to a $\pi$ state occur and that there is a discontinuity in the entropy at such transitions, which therefore are of first order. We calculate the corresponding latent heat, and find that its magnitude is observable given current experimental capabilities.

We study layered S/F systems containing a number $N_J$ of SFS junctions. We consider in particular $N_J = 1$, the important case of a single junction, and, to show the richness and variety of the possible outcomes, also the case $N_J = 3$. We compare as a function of $T$ the condensation free energies $\Delta F(T)$, defined as the difference $\Delta F(T) \equiv F_S(T) - F_N(T)$ between the free energies of the normal and superconductor states of each of the several possible self-consistent configurations. It is in principle very difficult to compute condensation free energies to the required accuracy: one needs only to recall that in the bulk and at zero $T$, $\Delta F$ equals $-(1/2)N(0)\Delta_0^2$ ($\Delta_0$ is the bulk gap). Since $F_N$ is much larger, of order $N(0)\omega_D^2$ ($\omega_D$ is the Debye frequency), $\Delta F$ is the small difference between two much larger quantities. Thus, one is faced with the tough numerical task of computing two quantities accurately enough so that the small difference between them can be reliably established. The problem is exacerbated for our systems because, as will be seen, the difference between the condensation free energies of the various possible states (e.g., the $0$ and $\pi$ cases for SFS trilayers) is at best a small fraction of their individual condensation free energies. The numerical methods we use do resolve these small differences. These calculations are carried out using the spectra and pair potentials obtained by fully self consistent numerical solution of the Bogoliubov deGennes (BdG) equations.

The systems studied here consist then of either 3 or 7 layers, containing 1 or 3 SFS junctions respectively. We denote the thickness of the F layers by $d_F$ and that of the S layers by $d_S$ and assume the interfaces are sharp. The procedures that we use to numerically solve the BdG equations for a clean system in a fully self consistent manner are detailed in Refs. 17,18 and the details need not be repeated here. As explained there, for many relevant values of the geometric and material parameters several self consistent solutions, that is, local minima of the free energy, often coexist at $T = 0$. For example, solutions of both the $0$ and $\pi$ type may be possible for one junction, while for the three junction case more than one of the possible symmetric states (000, $\pi\pi\pi$, $\pi0\pi$, and $0\pi0$ in the obvious notation denoting the state of each junction) may yield a self-consistent solution to the problem. In such cases, the equilibrium state had to be found by comparing the respective energies. It was shown that the symmetry of the stable solution at $T = 0$ can change as one varies parameters such as $d_F$, the interface barrier height, the exchange field of the magnet, or the Fermi wavevector mismatch between F and S materials. The switchover from one stable state to another occurs as the corresponding energies cross at certain points in parameter space: “phase transitions” take place as a function of such parameters. They may occur also in the dirty limit as a function of $d_F$. The issue is how these phenomena are related to transitions found experimentally at finite $T$.

Here we investigate the true thermodynamics, that is, how the equilibrium state of a given system depends on $T$, and the nature of the corresponding phase transitions. When self-consistent numerical solutions of the BdG equations are possible for multiple order parameter configurations, we evaluate the condensation free energies of the competing states. For this purpose we use the method of Ref. 21, which requires only the energy spectrum and the position dependent order parameter, but not the eigenfunctions. We find that in many cases there are first order phase transitions as a function of $T$, and that the latent heats are quite appreciable.

To locate phase transitions as a function of $T$, we searched near regions of parameter space where crossings occur at zero $T$. We focussed on the Fermi wavevector mismatch parameter defined as $\Lambda \equiv E_{FM}/E_{FS}$, where $E_{FS}$ is the Fermi energy (bandwidth) in the S material, while in F we have $E_k \equiv E_{FM} \pm h$ for the majority ($+$) and minority ($-$) bands. Here $h$ is the exchange field. We also considered the geometric parameter, $d_F$. For $N_J = 1$ we take $d_S$ equal to the zero temperature coherence length, $\xi_0$, while for $N_J = 3$ we double the thickness of the two inner S layers to $2\xi_0$. This mimics a more symmetric situation, since the outer layers are in contact with only one F layer. We measure energies in units of $E_{FS}$, lengths in units of $k_{FS}$, the Fermi wavevector for S, and set $k_{FS}\xi_0 = 100$. The strength of the magnet is chosen as $h = 0.2E_{FM}$ throughout. We assume that all magnetic layers are aligned and that there is no ox-
The normalized pair amplitude $F$ (see text) as a function of reduced temperature. The results in the top panel are for a one junction (SFS) system at $\Lambda = 0.535$ and $k_{FS}d_F = 7.5$. Results for the two possible order parameter configurations are plotted as indicated. Those in the bottom panel are for a three junction system at $\Lambda = 0.45$ and $k_{FS}d_F = 10$. Only the two lowest competing free energy configurations are plotted. The insets display the normalized pair amplitude $F(Z)$ at the transition points, where $Z \equiv k_{FS}z$.

Proceeding now to the results for $N_J = 2, 3$, the main plots in Fig. 1 show the condensation free energy $\Delta F$, as defined above, normalized by $N(0)\Delta_0^2$, which is twice the value of the condensation energy for a bulk S material at $T = 0$. In the top panel, $\Delta F$ is plotted versus reduced temperature $T/T_c^0$ for both the 0 and $\pi$ configurations of a 1 junction system. These results correspond to $k_{FS}d_F = 7.5$ and $\Lambda = 0.535$; similar results are found at this thickness for a range of $\Lambda$. Points at 0.01 intervals in the horizontal temperature scale are plotted, joined by straight segments. The slopes of the $\Delta F$ curves approach zero as $T \to 0$, which indicates zero entropy at $T = 0$. The slopes can also be seen to approach zero as $\Delta F \to 0$: thus we find that the transition to the normal state is second order, occurring at $T_c < T_c^0$. One can also see in the upper plot that the results for the 0 and $\pi$ states cross at $T_z/T_c^0 \approx 0.28$, with the $\pi$ configuration being the equilibrium state below $T_z$ and the 0 state above. The difference in the slopes at $T_z$ represents a latent heat, discussed below. Thus we predict that there is a transition and that it is first order. The inset displays the spatial profile of the corresponding pair amplitudes at $T_z$. The quantity plotted, $F(Z)$, is the pair amplitude as usually defined, normalized to its bulk S value at $T = 0$. $Z$ is the dimensionless distance $Z \equiv k_{FS}z$ normal to the layers. A discontinuity in the absolute value of $F(Z)$ at the transition can be noted.

The lower panel of Fig. 1 shows $\Delta F(T)$ similarly plotted for a 3 junction (7 layer) system with $k_{FS}d_F = 10$ and $\Lambda = 0.45$. Points are again taken at intervals of 0.01 on the horizontal scale. In this case only two ($\pi\pi\pi$ and $0\pi\pi$) of the possible configuration states compete as candidates for lowest free energy over the range of $T$ studied. The other possible states are therefore irrelevant and omitted. The curves in the lower panel display the same characteristics as in the 1 junction case: zero first derivatives as $T \to 0$, a second order transition to the normal state, and a first order transition at an intermediate $T$. In this case the transition is at $T_z/T_c^0 \approx 0.27$ and from a $\pi0\pi$ state at lower $T$ to $\pi\pi\pi$ at higher $T$. The inset again shows the corresponding $F(Z)$ at the transition. Thus in this more complicated example, the transition involves the inner 0 junction flipping to $\pi$ as $T$ is increased. Again, such first-order transitions exist...
over a range of $\Lambda$ at fixed $d_F$.

We can now derive the entire thermodynamics. Thus, Fig. 2 shows the dimensionless condensation entropies, $S(T)$, obtained by differentiating the results for $\Delta F(T)$ (Fig. 1) with respect to $T/T_c^0$. We show also the corresponding condensation energies, $U(T)$, computed from standard thermodynamic relations, normalized in the same way as $\Delta F$. In calculating the derivatives, a polynomial form was fit to the $\Delta F$ data in Fig. 1. The values found were equivalent to those obtained by taking a discrete derivative of the $\Delta F$ curves and fitting a polynomial to the resultant data. The top and bottom panels of Fig. 2 correspond, respectively, to the 1 and 3 junction cases in Fig. 1. As mentioned previously, the entropies go to zero smoothly as $T \to 0$ and $T \to T_c$. On the other hand, it is quite obvious that the transitions at $T_c$ (vertical arrows) are indeed first order: the entropies of the two states involved are not equal at that temperature. The condensation energy curves resemble those for a bulk superconductor. By taking a further derivative, the specific heat can also be obtained. For any given state the quantities $S(T)$, $U(T)$ and $\Delta F$ all go to zero at the same temperature, which is the computed value of $T_c$. The energies and entropies cross at temperatures above $T_c^0$: one can see that both entropy and energy play important and subtle roles in the first-order transition.

As one varies $\Lambda$, $T_c$ moves up or down smoothly and monotonically until the transition disappears when $T_c$ reaches either 0 or $T_c$. The difference between the entropies at $T = T_c$, which measures the latent heat, $L$, is quite appreciable and does not depend drastically on $T_c$ (nor equivalently on $\Lambda$) over most of the range. These points are illustrated in Fig. 3 where $L$ is shown for both the 1 and 3 junction systems. We show $L$ calculated as discussed in connection with Fig. 2 at several $T_x$, obtained by varying $\Lambda$. The sign of $L$ is defined by subtracting the entropy of the stable state below $T_x$ from that above $T_x$. So that the size of the effect can be appreciated, $L$ is normalized to the specific heat at $T_c^0$ of a normal S material of the same volume. This is appropriate since for a normal metal the specific heat at $T_c^0$ equals its entropy. One can see that, for both one and three junction samples, the entropy jumps at $T_c$ can exceed 1% of the entropy present in a uniform bulk S sample at $T_c^0$.

Translating these results for the normalized measure of the latent heat into actual units for typical samples, we find that they are of order of up to $10^{10} \text{kg} \cdot \text{K} / 10^{-13} \text{J}$. Standard ac calorimetry techniques offer a resolution at least one order of magnitude smaller. Indeed, even at-joule calorimetry has been achieved in electronic systems, although by using multiple samples. Our rigorous results are clearly larger than estimates made for dirty systems. These estimates, based on partial consideration of the Josephson energy only, are in the nature of lower bounds.

In summary, we have rigorously studied the thermodynamics of clean single and triple SFS junction systems. We have shown that as $T$ is varied a given junction can flip from the 0 state to the $\pi$ state. The resulting phase transition is first-order, in agreement with the experiments of Refs. 7,8,10, for systems with sharp interfaces. The associated latent heats were found to be within current experimental resolution. The results presented here should be applicable over a broad range of material parameters assuming $d_S$ does not exceed several $\xi_0$.

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