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Josephson-junction thermodynamics and the superconducting phase transition in a SQUID device

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In a model of two ideal BCS superconductors coupled by a tunneling Hamiltonian the nonvanishing of the Josephson internal energy (and entropy) for \( T \to T_c \) is shown to be a consequence of superconducting correlations, which persist in the thermodynamic limit even in the mean-field approximation. The ensuing rapid increase of the Josephson free energy as the temperature of a tunneling junction drops below the superconducting bulk transition temperature makes this transition of first order whenever the phase difference across the junction is fixed to a nonzero value. Taking this into account results in an availability potential governing the nonequilibrium thermodynamics of the junction which, in contrast with previously published results, has no unphysical features like latent heat released upon entering (or a superconducting phase dependent value in) the normal state. The analysis inter alia predicts a lowering of the critical temperature (to \( T_c' \)) for the junction, which has meanwhile been observed in high-quality superconducting quantum interference devices.

I. INTRODUCTION

The Josephson energy \( G_J(\phi, T) \) has the thermodynamic significance of a (Gibbs) free energy, for changes \( dG_J(\phi, T) \) are equal to electrical work \( V(\phi)J(\phi, T) \) done at constant temperature. Given an expression for \( G_J(\phi, T) \), one should thus be able to calculate the associated entropy \( S_J(\phi, T) = -\frac{\partial G_J(\phi, T)}{\partial \phi} \) and internal energy \( U_J = G_J + TS_J \). These quantities play an important role in the nonequilibrium thermodynamic theory of Josephson devices.\(^1-4\)

The Josephson entropy does not vanish as the temperature of the system approaches the bulk critical temperature \( T_c \) of the superconducting phase transition. Indeed, for one of the simplest formulas for \( G_J \) \(^{52} \) this entropy tends to a constant value, as the gap \( \Delta(\phi, T) \) decreases if \( T \to T_c^- \). The case is even more dramatic for a junction between unequal superconductors \( a \) and \( b \) \([\text{we take } (T_c)_a < (T_c)_b] \), where the phase-dependent part of \( G_J(\phi, T) \) is proportional to \( \Delta_a \Delta_b \), when \( \Delta_a \approx T \), and hence \( S_J \) even diverges if \( T \to (T_c)_a \).

While an entropy jump in itself is familiar from first-order transitions, presently \( S \) is greater in the low- than in the high-temperature phase, for \( \partial \Delta(T)/\partial T < 0 \). Hence, latent heat would be released upon entering the normal state, implying an unphysical instability.

The scenario can be studied in a superconducting quantum interference device (SQUID)\(^5-3\) by incorporating the junction in a superconducting ring. Indeed, the phase difference \( \phi = 2\pi \Phi/\Phi_0 \) (with \( \Phi_0 = h/2e \)) is externally controlled in a ring with negligible self-inductance so that the flux \( \Phi \) equals \( \Phi_{\text{ext}} \). We explain the mentioned instability, and show that for \( \phi \neq 0 \) the Josephson coupling lowers the actual \( T_c \), while the transition becomes first instead of second order.

In Sec. II we investigate the nonvanishing of the Josephson internal energy for \( T \to T_c^- \) in a model of two BCS superconductors coupled by a tunneling Hamiltonian. In Sec. III we explain the effect of the Josephson coupling on the superconducting transition, and examine the consequences for a theory of nonisothermal flux dynamics. The predicted decrease in \( T_c \) is estimated in Sec. IV. A detailed account is available in Ref. 5.

II. MICROSCOPIC THEORY

The system is modeled by the Hamiltonian

\[
H = H_0 + H_T = H_a + H_b + H_T, \tag{1}
\]

with \((c = a, b; \ V_c > 0)\)

\[
H_c = H_c,\text{kin} + H_c,\text{int}
= \sum_{p \alpha} \xi_p c_p^{\dagger} c_p - V_c \sum_{pp'} c_p^{\dagger} c_{-p}^{\dagger} c_{-p'} c_p' - p' \text{c.c.}, \tag{2}
\]

\[
H_T = \sum_{pq} T_{pq} c_p^{\dagger} b_q + H.c. \tag{3}
\]

We work in the grand canonical ensemble and the term \(-\mu N_c\) is included in \( H_c \), i.e., \( \xi_p = p^2/2m - \mu \). The prime on the sum implies restriction to \( p' \) with \( |\xi_{p'}| < \omega_D \), the Debye frequency. Neglecting the cutoff amounts to taking the
limit $\Delta_c, T \ll \omega_D \ll \mu$ (throughout $\hbar = k_B = 1$) and is allowed in all steps except when using the BCS gap equation to arrive at the last line of Eq. (18).

To introduce the Green’s functions $G_c$ of the uncoupled superconductors we define the Nambu field as
\begin{equation}
\Psi_c(p, \tau) = (c_p(\tau), -\bar{c}_{-p}(\tau))^T,
\end{equation}
so that
\begin{equation}
G_c(p, \tau) = -\langle \Psi_c(p, \tau) \Psi_c(-p) \rangle_0
= \left(\begin{array}{cc}
G_c(p, \tau) & F_c(p, \tau) \\
F_c^*(p, \tau) & -G_c(-p, -\tau)
\end{array}\right)
\end{equation}
yields
\begin{equation}
G_c(p, \omega) = \frac{1}{\omega^2 + \xi_p^2 + \Delta_c^2} \left(\begin{array}{cc}
-\omega - \xi_p & \Delta_c e^{i\phi_c} \\
\Delta_c e^{-i\phi_c} & -\omega + \xi_p
\end{array}\right),
\end{equation}
$\Delta_c$ being the magnitude of the gap.

In Nambu notation the tunneling Hamiltonian reads
\begin{equation}
H_T = \sum_{pq} \bar{\Psi}_a(-p) T_{pq} \Psi_b(q) + H.c.,
\end{equation}
where
\begin{equation}
T_{pq} = \text{diag}(T_{pq}, -T_{q-p}).
\end{equation}

Evaluating the change in grand canonical potential due to tunneling in lowest-order perturbation theory one finds
\begin{equation}
\delta G = G(T_{pq}) - G(T_{pq} = 0)
= \frac{1}{2} T \int_0^\beta \int_0^\beta d\tau_1 d\tau_2 \langle T_T[H_T(\tau_1)H_T(\tau_2)] \rangle_0
= T \sum_{pq} \text{Tr} \{G_c(p, \tau_2 - \tau_1) T_{pq} G_b(q, \tau_1 - \tau_2) T_{pq}^\dagger \}
= T \sum_{pq\omega} \text{Tr} \{G_a(p, \omega) T_{pq} G_b(q, \omega) T_{pq}^\dagger \},
\end{equation}
where we used Eq. (8) for $H_T$ and applied Wick’s theorem. To evaluate Eq. (10), we assume that the tunneling amplitudes obey time-reversal symmetry $T_{pq} = T_{pq} T_{3}$ and are energy independent (on the scale of $T_c$). Decomposing the sum over $p$ as $\sum_p = \sum_n (0)^\dagger \sum_{\xi_p} (d_p/4\pi)$ [where the approximation $N_b(\xi_p) \approx N_b(0)$ is correct first order in $(T_c/\mu)\gamma$, the integrals over $\xi_{p,q}$ can be performed with $G_a,b$ as in Eq. (7)]. This yields
\begin{equation}
\delta G = -2T \gamma \sum_{pq \omega} Q P^{-1},
\end{equation}
with $P = \sqrt{\omega^2 + \Delta_a^2}, Q = \omega^2 + \Delta_c \Delta_a \cos \phi$ ($\phi = \phi_a - \phi_b$), and the dimensionless conductance
\begin{equation}
\gamma = \pi^2 \langle (T_{pq})^2 \rangle N_a(0) N_b(0) = \pi/(4e^2 R^N),
\end{equation}
the relation between the tunneling amplitudes and the normal-state resistance $R^N$ being standard.\(^7\)

The sum in Eq. (11) diverges for $\delta G$, but converges for its difference between the superconducting and normal states $\delta G_{S-N} = \delta G_S - \delta G_N$, which is the quantity of interest. A general property is its nonnegativity: $\delta G_{S-N} \approx \sum_{\omega}(1-Q/P) \geq 0$ because
\begin{equation}
P^2 - Q^2 \geq (\omega^2 + \Delta_a^2)(\omega^2 + \Delta_b^2) - (\omega^2 + \Delta_a \Delta_b)^2
= \omega^2 (\Delta_b - \Delta_b)^2 \geq 0.
\end{equation}
For equal gaps $\Delta_a = \Delta_b = \Delta$ one finds (see Ref. 7)
\begin{equation}
G_T = \delta G_{S-N} = 2T \gamma \Delta^2 (1 - \cos \phi) \sum_{\omega} (\omega^2 + \Delta^2)^{-1}
= \gamma \Delta \tanh(\Delta/2T)(1 - \cos \phi),
\end{equation}
consistent with Anderson’s theorem,\(^8\) implying that $G_T(\phi = 0) = 0$ (to lowest order in $T_c/\mu$), which will be crucial in Sec. III.

For unequal gaps $\Delta_a, \Delta_b \ll T$ one obtains
\begin{equation}
G_T = \frac{\gamma}{4T}(\Delta_a^2 + \Delta_b^2 - 2 \Delta_a \Delta_b \cos \phi) + O[(\Delta/T)^4],
\end{equation}
while for two superconductors with very different $T_c$ near the lower of these temperatures, i.e., for $\Delta_a \ll T \ll \Delta_b$, the result reads\(^3\) ($\gamma_E$ is Euler’s constant)
\begin{equation}
\gamma^{-1} G_T = \frac{2}{\pi} \Delta_b - \frac{\pi T^2}{3 \Delta_b}
+ \frac{1}{\pi} \left[ \frac{\Delta_a^2}{\Delta_b} - 2 \Delta_a \cos \phi \right] \left[ \ln \frac{4\Delta_b}{\pi T} \right] + \gamma_E
+ T \left[ O((T/T_c)^3) + O(T\Delta_a/\Delta_b^2 + O((\Delta_a/T)^3)) \right].
\end{equation}

Since $\Delta_{a,b} \gg \sqrt{(T_c/a)_{a,b} - T}$ for $T \ll (T_c/a)_{a,b}$, with $U = \delta G_B(\delta G)$ the above formulas for $G_T$ predict a constant [Eq. (13)] or even divergent [Eqs. (14) and (15)] internal energy (and entropy) difference $\delta U_{S-N}$ upon approaching the (lowest) $T_c$ from below. This property is a consequence of deviations from BCS mean-field theory (even though these superconducting correlations are of order $N_{a,b}$), as is demonstrated by an explicit calculation of $\delta U$ in which such correlations are neglected. Consider
\begin{equation}
\delta U = \delta \langle H_a \rangle + \delta \langle H_b \rangle + \langle H_T \rangle,
\end{equation}
where $\delta \langle \cdot \rangle = \langle \phi \rangle - \langle \cdot \rangle_0$. In first order $\langle H_T \rangle = 2\delta G$, with $\delta G$ as in Eq. (10). For $\langle H_a \rangle$ one has
\begin{equation}
\langle H_a \rangle = \sum_{p,a} \xi_p a_p^\dagger a_p - V \sum_{pp'} \langle a_p^\dagger a_{-p}^\dagger a_p a_{-p'} \rangle.
\end{equation}
Expanding the second term in terms of two-point functions, the Hartree-Fock contribution to $\delta \langle H_a \rangle_{MF}$ vanishes in the thermodynamic limit. One is left with
where we used $\delta(a_0^{(1)} a_{-p}^{(1)}) = O[N_0^{-1}]$ so that only the linear term contributes to $\delta(H_a)$. To evaluate the rhs of Eq. (18) in lowest order transform to frequencies, and use $\Delta_a e^{i\phi_a} a^{(1)}_{-p} = G_a(p, \omega)^{-1} - i\omega$ to arrive at

$$\delta(H_a)_{MF} = \sum_{pq\omega} \mathrm{Tr}\{ [i \omega - G_a(p, \omega)]^{-1} \}$$

$$\times G_a(p, \omega) T_{pq} G_b(q, \omega)^t T_{pq} G_a(p, \omega) \}$$

$$= -T \sum_{pq\omega} \omega \mathrm{Tr}\{ (\delta_a G_a(p, \omega)) T_{pq} G_b(q, \omega)^t T_{pq} \}$$

$$- \frac{1}{ \beta} \langle H_\beta \rangle,$$  

(19)

$\delta(H_a)$ following by symmetry. Substitution into Eq. (16) shows that $\langle H_\beta \rangle$ cancels in $\delta U_{MF}$, viz.,

$$\delta U_{MF} = -T \sum_{pq\omega} \omega \partial_\omega \mathrm{Tr}\{ G_a(p, \omega) T_{pq} G_b(q, \omega)^t T_{pq} \}$$

$$= \hat{\beta}_{ab} \sum_{pq\omega} \mathrm{Tr}\{ G_a(p, \omega) T_{pq} G_b(q, \omega)^t T_{pq} \}$$

$$= \hat{\beta}_{ab} \beta \delta G_{a,b}.$$

(20)

As our derivation is valid in the normal (N) and the superconducting (S) phase, this relation also holds between $\delta U_{MF}^{S-N}$ and $\delta U_{MF}^{G-S-N}$. By Eqs. (13)–(15) and (20), $\delta U_{MF}^{S-N}$ vanishes as $T \rightarrow T_c$, which is what we set out to show.

**III. THERMODYNAMICS**

The free energy of the system (with respect to the N state) also contains the phase (or SQUID flux) independent bulk condensation energy, which is quadratic in $T_c - T$ near $T_c$. It usually completely dominates the Josephson term $G_\beta [\equiv 0$ by virtue of Eq. (12)]. Accounting for the bulk energy is crucial for resolving the thermodynamic instability of the junction below $T_c$ (see Sec. I).

For a fixed $\phi \neq 0$, $G^{S-N}$ varies with temperature as in Fig. 1. Just below $T_c$ the total free energy in the S phase is higher than in the N phase, so that the system remains in the state $\Delta = 0$ (always a solution of the gap equation) until $G^{S-N} = 0$ again, at $T_c'$ [see Eq. (24)]. At this $T_c' < T_c$, $\Delta$ jumps to a finite value. This first-order transition is indeed accompanied by latent heat (see Sec. I), as follows from the kink in $G(T)$. The significance of Anderson's theorem (see Sec. II) is that the transition remains of second order if no flux is applied externally.

Now consider the nonequilibrium thermodynamics of the system (see Refs. 1–3). Equation (19) of Ref. 3 and the one below it yield

$$A = -E_0 \cos \left( \frac{2\pi}{\Phi} \right) \left[ 1 - \frac{3T^2 - 2T^3}{T_c^3} \right] + \frac{2L}{\alpha^2} T_c^3$$

(21)

for the availability $A = G + (T - T_c) S$ of a SQUID in contact with a bath at temperature $T_c$. Here $E_0 = I_c (T_c = 0) / 2e$, $\alpha$ arises in a Debye-type bulk free energy $G_{bulk} = -\alpha (T/T_c)^3$, and $T = \min(T, T_c)$. Following Eq. (21), an availability barrier persists in the N state near $\Phi = \frac{1}{2} \Phi_0$. However, this barrier is entirely due to the Josephson coupling and related to the unphysical negative latent heat discussed in Sec. I. This artifact is remedied by accounting for the bulk condensation energy, which we now model à la Refs. 1–3. Since Eq. (21) implies $S_{bulk} = \frac{1}{2} \alpha T_c^2$, we take $S_{bulk}^{S-N} = \frac{1}{2} (\alpha/2) (T/T_c)^2 + \eta (\eta > 0)$. For the $S^-$ phase one obtains

$$S_{bulk}^{S^-}$$

FIG. 1. The Josephson, bulk and total free energy of a junction with $\phi \neq 0$ (arbitrary units). The dashed line indicates the free energy of the superconducting phase, the thick line the equilibrium free energy $G(T)$.
while $A^N$ follows from Eq. (22) with $E_i = \eta = 0$. The free energy $G^{SN}$ results from $A^{SN}$ by setting $T_i = T$. Our final result for $A(T)$ then follows from

$$A(T) = \{\theta(T - T_c) + \theta(T_c - T) \theta(G^S(T) - G^N(T))\}A^N(T)$$

$$+ \theta(T_c - T) \theta(G^N(T) - G^S(T))A^S(T). \tag{23}$$

A calculation of the junction’s actual critical temperature $T'_c$ (see above in this section) is now easy in the limit $E_i \ll \alpha$, in which the effect of the Josephson coupling is small and hence $\varepsilon = (T'_c - T_c)/T_c \ll 1$. Expansion of $G^S = G^N$ in $E_i/\alpha \ll 1$ yields

$$\varepsilon = \frac{12E_i}{\alpha \eta} \left[ 1 - \cos \left( 2\pi \frac{\Phi}{\Phi_0} \right) \right]. \tag{24}$$

IV. FINAL REMARKS

The thermodynamic analysis of Sec. III can also be motivated in the context of a dynamical theory of nonisothermal behavior, which has potential relevance for a wide class of physical systems. The relevant “reaction coordinate” (here the flux) and the temperature then become fluctuating quantities, the values of which spread over the entire accessible state space. Hence, there is no a priori possibility to restrict the variables to a bounded region such as $T < T_c$ (or $T > T_c$), so that covering the phase transition becomes crucial.

Of course, the phenomenology of Sec. III is no substitute for solving Gor’kov equations for a finite-size SQUID. Also, the model (1) obscures the fact that tunneling is an interface phenomenon. However, this should allow a Ginzburg-Landau description near $T_c$, e.g., to determine the effective interaction volume $V$ (see below).

To estimate $T'_c$, take $\Phi = \frac{1}{2}\Phi_0$ and $E_i = h\Delta(0)/8e^2R^N \approx 10^{-19}/R^N$ J (for Al) in Eq. (24). From Eq. (22) we find $G_{bulk}^N = \frac{4}{3}\alpha \eta (1 - T/T_c)^2$, which yields $\alpha \eta \approx 6V\beta_3(0)^2/\mu_0$, upon comparison with $G_{bulk}^S = (V/2\mu_0)(1.73B_3(0)(1 - 1/T_c))^2$ [Ref. 6, Eq. (36.12)], where $\mu_0 = 4\pi \times 10^{-7}$ H m$^{-1}$ and $\beta_3(0) \approx 10^{-2}$ T [for Al (Ref. 10)], so that $\varepsilon \approx 5 \times 10^{-2} / VR^N$. For $V = 0.1 \mu m^3$ and $R^N = 50 \Omega$, one arrives at $\varepsilon \approx 10^{-3}$. With $T_c \approx 1$ K this means that the effect is in the mK range, and hence observable in state-of-the-art devices of sufficiently small dimensions and of a high material quality such that $T_c$ is sharply defined.

In conclusion, this work highlights hitherto neglected consequences of the phase-independent part of the Josephson coupling [the first term in Eq. (13)], which near $T_c$ is not an arbitrary constant. In the meantime, its predictions concerning the oscillations of $T_c$ versus the applied magnetic flux in a SQUID device have indeed been confirmed experimentally.11

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6A.A. Abrikosov, L.P. Gor’kov, and I.E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics (Dover, New York, 1975).


9The relative stability of phases can also be determined in terms of the availability (instead of $G$), but then $A$ has to be considered as a function of the enthalpy and the analysis becomes more involved; see further Ref. 5.
