Inconsistency of the conventional theory of superconductivity

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In a process where the temperature of a type I superconductor in a magnetic field changes, the conventional theory of superconductivity predicts that Joule heat is generated and that the final state is independent of the speed of the process. I show that these two predictions cannot be simultaneously reconciled with the laws of thermodynamics. I propose a resolution of this paradox.

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I. INTRODUCTION

Within the conventional London-BCS theory of superconductivity [1], the state of a simply connected superconductor in an external magnetic field is independent of how the system reached that state. The theory also predicts that when an electric field exists in a superconductor at finite temperature, Joule heat is always generated. Here I point out that for a type I superconductor in the presence of a magnetic field, those two assumptions lead to a contradiction with the laws of thermodynamics in a process where the temperature is changed below T_c. Consequently, one of the two assumptions must be incorrect in that situation. I propose it is the second one, and that the alternative theory of hole superconductivity offers a possible resolution of this paradox.

II. THE PROCESS

Figure 1 shows the phase diagram of a type I superconductor in a magnetic field H [1]. We consider the process where a cylindrical superconductor is cooled from state 1 to state 2 shown in Fig. 1, in the presence of an applied field H_0. The inconsistency also arises if we consider heating instead. The magnetic field of a long cylinder of radius R and London penetration depth λ_L in a magnetic field H_0 parallel to its axis is [2]

$$\vec{B}(r) = H_0 \frac{J_0(ir/\lambda_L)}{J_0(iR/\lambda_L)} \hat{z} \tag{1}$$

where J_0 is the Bessel function of order 0 and $\hat{z}$ is along the cylinder axis. To lowest order in λ_L/R,

$$\vec{B}(r) = H_0 e^{(r-R)/\lambda_L} \hat{z}. \tag{2}$$

The London penetration depth is a decreasing function of temperature, hence a decreasing function of time in the process of cooling. In the process shown in Fig. 1, the London penetration depth changes from λ_1 to $\lambda_2 < \lambda_1$ when the temperature is lowered from T_1 to T_2. Figure 2 shows the superconductor as seen from the top, with the dots indicating magnetic field pointing out of the paper.

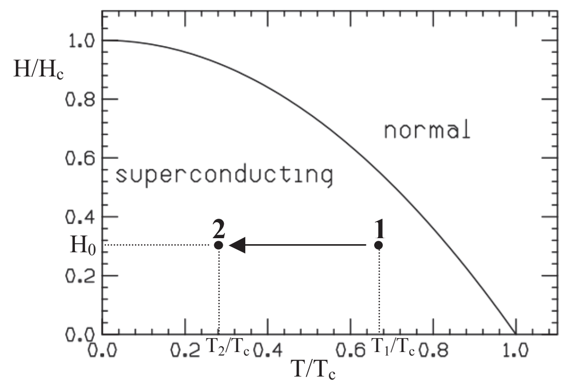

FIG. 1: Critical magnetic field versus temperature for a type I superconductor. We will consider the process where a system evolves from point 1 to point 2 along the direction of the arrow.

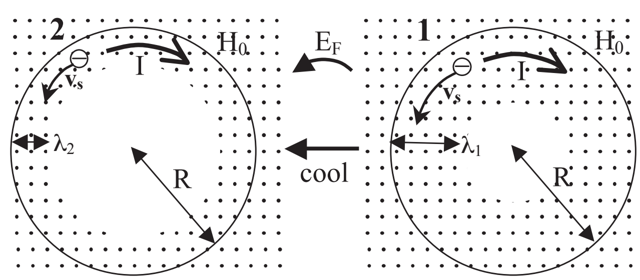

FIG. 2: Cylindrical superconductor seen from the top. The right (left) panel indicates the system in the state 1 (2) of Fig. 1. The dots indicate magnetic field H_0 coming out of the paper. The same current I flows in both states. The Faraday electric field E_F generated during the process points counterclockwise.

III. FARADAY ELECTRIC FIELD

The magnetic field near the surface is changing in this process, therefore a Faraday electric field is generated. We assume cylindrical symmetry throughout the process. The electric field at radius r at time t is determined by the equation

$$\oint \vec{E}(r,t) \cdot d\vec{\ell} = -\frac{1}{c}\frac{\partial}{\partial t}\int_{r'<r} \vec{B}(r',t) \cdot d\vec{S} \tag{3}$$

which yields

$$\vec{E}(r,t) = -\frac{H_0}{c}(1+\frac{R-r}{\lambda_L})e^{(r-R)/\lambda_L(t)}\frac{\partial\lambda_L}{\partial t}\hat{\theta}. \quad (4)$$

The electric field points counterclockwise.

At any given temperature there are both superfluid and normal electrons, of density n_s and n_n, with $n_s + n_n = n$ constant in time, in a two-fluid description [1]. Similarly within BCS theory there is the superfluid and Bogoliubov quasiparticles at finite temperature, we will call the latter 'normal electrons' [1]. The Faraday electric field will impart momentum to these normal electrons during the process, and this momentum will decay to zero through scattering with impurities or phonons [1]. These are irreversible processes, that generate Joule heat and entropy [3]. The normal current induced by the Faraday electric field is

$$j_n(r,t) = \sigma_n(t)E(r,t) \quad (5)$$

with [1]

$$\sigma_n(t) = \frac{n_n(t)e^2\tau}{m^*} \quad (6)$$

within a Drude description with relaxation time τ, with m^* the transport effective mass. The energy dissipated per unit time per unit volume is

$$\frac{\partial w(r,t)}{\partial t} = \sigma_n(t)E(r,t)^2, \quad (7)$$

and the energy per unit time dissipated over the entire volume is

$$\frac{\partial W(t)}{\partial t} = \int d^3r \frac{\partial w(r,t)}{\partial t}. \quad (8)$$

If the process extends from time $t = 0$ to $t = t_0$ the total Joule heat dissipated is

$$Q_J = \int_0^{t_0} \frac{\partial W(t)}{\partial t} dt \quad (9)$$

and the Joule entropy generated during this process is

$$S_J = \int_0^{t_0} \frac{\partial W}{\partial t}\frac{1}{T(t)} dt \quad (10)$$

where $T(t)$ is the temperature at time t. We assume the process is sufficiently slow that $T(t)$ is well defined at all times.

Note that Q_J and S_J depend on the speed of the process. If we assume for simplicity that $\partial\lambda_L/\partial t$ is constant, we have

$$\int_0^{t_0} (\frac{\partial\lambda_L}{\partial t})^2 F(\lambda_L(t))dt = \frac{\partial\lambda_L}{\partial t}\int_{\lambda_1}^{\lambda_2} F(\lambda_L)d\lambda_L \quad (11)$$

for any F, so Q_J and S_J are directly proportional to $\partial\lambda_L/\partial t$. In addition, Q_J and S_J are proportional to the Drude relaxation time τ, or equivalently to the normal state conductivity.

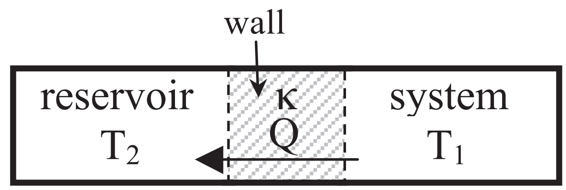

FIG. 3: The system (superconductor in a magnetic field) at initial temperature T_1 is connected to a heat reservoir at temperature $T_2 < T_1$ through a wall of thermal conductivity κ. The entire assembly is thermally and mechanically insulated from its environment.

IV. THERMODYNAMICS

We consider the situation shown in Fig. 3. The system is our superconductor with phase diagram given in figure 1, with applied magnetic field H_0. The system is initially in thermal equilibrium at temperature T_1, with London penetration depth $\lambda_1 = \lambda_L(T_1)$.

We put it in thermal contact with a heat reservoir at temperature $T_2 < T_1$ through a wall with thermal conductivity κ. Heat will flow and eventually the system will reach temperature T_2 and be in thermal equilibrium with the heat reservoir. We assume the entire assembly is thermally and mechanically insulated from its environment. The magnetic field originates in external permanent magnets, no work is performed on those magnets during the process. We also assume the process is sufficiently slow that no electromagnetic radiation is generated. Under these conditions, *the initial and final states of BOTH the system AND the reservoir are uniquely determined.*

Given the initial and final states, we can compute various thermodynamic quantities. The total heat Q transferred from the system to the reservoir during the process is

$$Q = \int_{T_2}^{T_1} dTC(T) \quad (12)$$

where $C(T)$ is the equilibrium heat capacity of our system. The change in entropy of the system in this process is

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} dT\frac{C(T)}{T} \quad (13)$$

and is of course negative since $T_2 < T_1$. The change in entropy of the universe in this process is

$$\Delta S_{univ} = \frac{Q}{T_2} + \Delta S \quad (14)$$

and is of course positive since we are dealing with an irreversible process, heat conduction between systems at different temperatures. The quantities Q and ΔS_{univ} depend *only* on the initial and final states of the process, *not* on the speed at which the process happens.

The Joule heat Q_J and associated entropy S_J discussed in the previous section depend on the speed of the process, which will depend principally on the thermal conductivity of the heat conductor, κ, connecting the system and the heat reservoir. It would appear that the existence of Joule heat violates both the first and second law of thermodynamics.

In the next section we will show that even if it may be possible to 'save' the first law by some contrived assumption, the second law is necessarily violated.

V. THE INCONSISTENCY

Let us consider a small step in the process, starting with the system at temperature T, where the system supplies heat ΔQ to the reservoir which is at temperature $T_2 < T - \Delta T$. The system will change its temperature from T to $T - \Delta T$. Assume we connect and disconnect the thermal connection between system and reservoir at the beginning and the end of this step, and wait at the end until equilibrium has been attained. Consider two different ways to do this step:

(a) Infinitely slowly

(b) In a finite amount of time, Δt.

According to the previous discussion, for (b) finite Joule heat will be generated in the system during this process.

First, let's realize that the change in temperature of the system, ΔT, has to be the same for (a) and (b). The reason is, the energy transferred to the reservoir was ΔQ for both (a) and (b), and the final state and hence final temperature of the system is uniquely determined by its energy, which is the same for (a) and (b), namely (initial energy -ΔQ). Note also that the energy in the electromagnetic field is also the same in the final state of processes (a) and (b). We discuss the electromagnetic field in detail elsewhere [4], it is not necessary to include it for this argument. The final state of the reservoir is also unique, depending only on the amount of heat ΔQ supplied to it, and independent of the speed at which that heat was supplied to it.

For process (a), we have

$$\Delta Q = C(T)\Delta T \tag{15}$$

where $C(T)$ is the equilibrium heat capacity of the system. For process (b), assume Joule heat ΔQ_J is generated. One could imagine that the heat capacity of the system is different than the equilibrium one when the process occurs at a finite rate and involves Joule heat, let's call it $C_r(T) < C(T)$. We will then have for process (b)

$$\Delta Q = C_r(T)\Delta T + \Delta Q_J \tag{16}$$

transferred from the system to the reservoir, the same as in process (a). So under this assumption the first law of thermodynamics is not violated, energy is conserved.

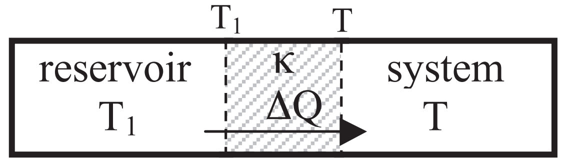

FIG. 4: Heating: the reservoir is at temperature T_1, the system is at temperature $T < T_1$. An amount of heat ΔQ flows from the reservoir to the system in a time t_0 that is inversely proportional to κ and to $(T_1 - T)$.

However, let's consider the change in entropy of the universe. In process (a) it is

$$\Delta S_{univ}^{(a)} = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T} + O((\Delta T)^2). \tag{17}$$

In process (b), Joule heat ΔQ_J is generated. Quantitatively, we obtain from Eqs. (4), (7) and (8)

$$\frac{\partial W}{\partial t} = \sigma_n \left(\frac{\partial \lambda_L}{\partial t}\right)^2 \frac{H_0^2}{c^2} \frac{\pi h R \lambda_L(t)}{2} \tag{18}$$

and $\Delta Q_J = \int (\partial W/\partial t) dt$ is given by

$$\Delta Q_J = \Delta T \frac{\kappa A}{C(T)} \frac{T - T_2}{d} \frac{\lambda_L(T)}{2R} \sigma_n \left(\frac{\partial \lambda_L}{\partial T}\right)^2 \frac{H_0^2}{c^2} V \tag{19}$$

where we used that

$$\frac{\partial T}{\partial t} = \frac{\kappa A}{C(T)} \frac{T - T_2}{d}. \tag{20}$$

$V = \pi R^2 h$ is the volume of the cylinder, d the thickness of the wall connecting the reservoir and system and A its area, and σ_n is given by Eq. (6) with $n_n(T)$.

Therefore, in process (b) entropy increases for two reasons. First, generation of Joule heat generates entropy:

$$\Delta S_J = \frac{\Delta Q_J}{T} + O((\Delta T)^2). \tag{21}$$

Note that ΔQ_J and hence ΔS_J is $O(\Delta T)$ and not $O((\Delta T)^2)$. Second, the transfer of the heat ΔQ from the system to the reservoir generates the same entropy as given by eq. (17), which is also $O(\Delta T)$. Therefore, the change in entropy of the universe in process (b) is

$$\Delta S_{univ}^{(b)} = \Delta S_{univ}^{(a)} + \Delta S_J > \Delta S_{univ}^{(a)}. \tag{22}$$

However, entropy is a function of state. Therefore, the second law of thermodynamics is violated by Eq. (22).

We can also consider the reverse process, heating the superconductor below T_c, as shown in Fig. 4, where the inconsistency may be even clearer. With the system at temperature $T < T_1$, with T_1 the temperature of the reservoir, an amount of heat ΔQ will flow from the reservoir to the system and raise the temperature of the system by $\Delta T = \Delta Q/C(T)$. The change in entropy of the universe in this process if it occurs infinitely slowly (i.e. if $\kappa \to 0$) is

$$\Delta S_{univ} = -\frac{\Delta Q}{T_1} + \frac{\Delta Q}{T} + O((\Delta T)^2). \quad (23)$$

The time the process actually takes for finite κ is finite, inversely proportional to κ and to $T_1 - T$. The Joule heat generated ΔQ_J is given by Eq. (19) with $(T_1 - T)$ replacing $(T - T_2)$. We have to assume that through an unspecified process, which itself may violate the second law, a part of the absorbed ΔQ, in an amount that depends on κ, is used up in providing the work that propels the normal current, that decays by generation of ΔQ_J. In any event, Joule entropy

$$\Delta S_{extra} = \frac{\Delta Q_J}{T} + O((\Delta T)^2) \quad (24)$$

will be generated by the decay of the normal current that is added to the entropy Eq. (23), violating the second law.

VI. IS THERE A POSSIBLE RESOLUTION WITHIN THE CONVENTIONAL THEORY?

It has been suggested that one crucial flaw (1) in my argument may be the implicit assumption that the sample at intermediate times can be characterized by a uniform temperature T [5]. Another flaw (2) may be that even assigning a well-defined temperature to the region where normal current is flowing may not be possible [5]. Another possible flaw (3) may be that the relaxation time may be a function of momentum in the superconducting state rendering Eq. (5) invalid [6], and another flaw (4) may be that assuming that the only dissipative mechanism in the problem is the Joule heating may render my conclusion invalid [6]. In the following I address those suggestions.

Regarding (3) and (4), I argue that even if those suggestions are valid they would not invalidate my argument. If there is another dissipative mechanism in the problem besides Joule heating (and in fact I believe there is within the conventional theory [7]) it would only make the inconsistency worse, since all I need is that there is some dissipation for the inconsistency to arise. Regarding Eq. (5), even if it needs to be replaced by a more complicated expression that would take into account a relaxation time that is a function of momentum and/or a non-local generalization of Ohm's law, it would not change the fact that it gives rise to dissipation. Furthermore, as discussed by Tinkham [1], Sect. 2.5, a two-fluid approximation with a normal conductivity given by Eq. (5) "is the standard working approximation for understanding electrical losses in superconductors" in situations with ac currents or applied electromagnetic fields, and there is no reason to expect within the conventional theory that the same would not apply to the situation considered here.

The most serious objection may be (1), that the sample may not be at a uniform temperature. Let us examine that suggestion. First, I would argue that the speed at which temperature equilibrates depends on another variable not included in the argument, namely the thermal conductivity of the sample, that is at our disposal. We may simply assume we have a sample with sufficiently high thermal conductivity that it homogenizes the temperature on a timescale much shorter than all other timescales in the problem.

Still, let us assume that for some unknown reason this does not happen. Considering the heating process of Fig. 4, let us assume the surface layer heats up and becomes hotter than the bulk, and becomes a 'subsystem' at temperature $T_h = T + \delta T$. One might argue that part of the incoming heat ΔQ provides energy to drive the Joule current in this subsystem at temperature T_h, and the resulting Joule heat is dumped into the bulk at the lower temperature T as in a 'heat engine', thus not violating the second law. The heat coming into the subsystem at temperature T_h would raise its entropy less than if its temperature was T, and this difference may account for the extra Joule entropy generated.

To counter this argument, we may simply assume that the sample is not heated from the surface but from the interior. Assume the sample is a hollow cylinder, with no magnetic field in the interior nor in the hollow cavity, so that supercurrent only flows near the outer surface as before. The heat ΔQ is added through the inner surface, so there is no mechanism for the outer surface layer to heat up beyond the bulk before generating Joule heat. As the heat ΔQ is coming in, the London penetration depth will increase, with a corresponding change in magnetic flux and associated Faraday field generated, and the generated Joule heat ΔQ_J will generate Joule entropy $\Delta Q_J/T$ thus violating the second law.

Finally, regarding the suggestion that assigning a well-defined temperature to the region where normal current is flowing may not be possible, I would simply say that even if so it does not eliminate the inconsistency. Particularly in the scenario described in the preceding paragraph. Furthermore one has to keep in mind that the thickness of the region where the current flows could even be a significant fraction of the volume of the system, at temperatures sufficiently close to T_c and with sufficiently small magnetic fields, and if the thermal conductivity of the sample is large and the process not very fast there is no reason to assume that a large portion of the system would have an undefined temperature. Note that it is sufficient that there is one situation where the inconsistency clearly exists to validate our argument. Achilles' heel doesn't have to be more than a tiny fraction of the entire body area.

VII. DISCUSSION

The Faraday electric field is a consequence of Maxwell's equations and is unavoidable. The fact that electric fields in superconductors give rise to dissipation is well known from experiments with ac currents or electromagnetic waves incident on superconductors [8], and is predicted by BCS theory [8]. So how can this inconsistency be resolved?

If the processes occurs always infinitely slowly, the Joule heat and associated entropy go to zero and the inconsistency is resolved. However, there is no mechanism to make these processes proceed infinitely slowly if κ is large. Furthermore, we know from experiments that superconductors in magnetic fields can be cooled or heated and reach equilibrium states at the new temperatures in finite time.

Another way to resolve this inconsistency would be to assume that the final state depends on the process. Neither I nor (I suspect) anybody else is willing to go back to that notion, that was discarded in 1933. The contrary notion is an integral part of the conventional theory.

I argue that the only other way to resolve this inconsistency is to assume that in the particular situation considered here, where the electric field arises from a change in temperature, the superconductor behaves differently than in other situations with electric fields, namely here no normal current is generated and no dissipation takes place.

That is not predicted by the conventional theory [1]. In addition, within the conventional theory that is impossible, for the following reason. From Ampere's law,

$$\oint \vec{B} \cdot d\vec{\ell} = \frac{4\pi}{c} I \tag{25}$$

where I is the total current, yielding

$$I = \frac{c}{4\pi} h H_0. \tag{26}$$

where h is the height of the cylinder. Therefore, the total current I is independent of temperature. However, the Faraday electric field transfers momentum to the supercurrent, as well as to the body as a whole. In order for the current to stay the same, there has to be a mechanism for momentum transfer between electrons and the body as a whole.

Within the conventional theory of superconductivity, the only way to transfer momentum between electrons and ions is through scattering processes involving normal electrons, the same processes that give rise to normal resistivity and Joule heat in the normal state [9]. If these processes occur at a finite rate as in the situation considered here, finite Joule heat and Joule entropy will necessarily be generated. Therefore, the inconsistency cannot be resolved within the conventional theory.

The only way to transfer momentum between electrons and ions without dissipation other than infinitely slowly is if electrons have negative effective mass. If so, an external force acting on the electron gives rise to acceleration in opposite direction to the force because the difference in momentum is transferred to the body, without scattering processes and associated dissipation.

This then implies that to resolve the inconsistency pointed out in this paper charge carriers in superconductors have to be holes [10] rather than electrons. This is not required within the conventional theory but is required within the alternative theory of hole superconductivity [11]. We have shown that within that theory there is momentum transfer between electrons and ions without dissipation in the normal-superconductor and superconductor-normal transitions in the presence of a magnetic field [7, 12, 13].

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