Thermodynamic inconsistency of the conventional theory of superconductivity

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A type I superconductor expels a magnetic field from its interior to a surface layer of thickness λ_L, the London penetration depth. λ_L is a function of temperature, becoming smaller as the temperature decreases. Here we analyze the process of cooling (or heating) a type I superconductor in a magnetic field, with the system remaining always in the superconducting state. The conventional theory predicts that Joule heat is generated in this process, the amount of which depends on the rate at which the temperature changes. Assuming the final state of the superconductor is independent of history, as the conventional theory assumes, we show that this process violates the first and second laws of thermodynamics. We conclude that the conventional theory of superconductivity is internally inconsistent. Instead, we suggest that the alternative theory of hole superconductivity may be able to resolve this problem.

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I. INTRODUCTION

After the discovery of the Meissner effect, it was concluded that the superconducting state of a simply connected body in the presence of a magnetic field lower than the critical field is a thermodynamic state of matter and not a metastable non-equilibrium state that depends on history, as was previously believed [1]. Conventional superconductors are believed to be described by London theory and BCS theory, which we will call the conventional theory [2]. In this paper we show that the conventional theory cannot describe certain processes in type I superconductors without violating well established laws of physics.

Figure 1 shows the phase diagram of a type I superconductor in a magnetic field H. 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. Figure 2 shows the superconductor as seen from the top, with the dots indicating magnetic field pointing out of the paper. We will discuss the details in the following. We will conclude that the conventional theory is inconsistent with the laws of thermodynamics.

II. BASIC EQUATIONS IN SIMPLEST FORM

We consider a long cylinder of radius R and height h, with $R << h$, in an applied uniform magnetic field H_0 parallel to its axis. Assume the cylinder is in the superconducting state, hence the magnetic field in the deep interior is zero.

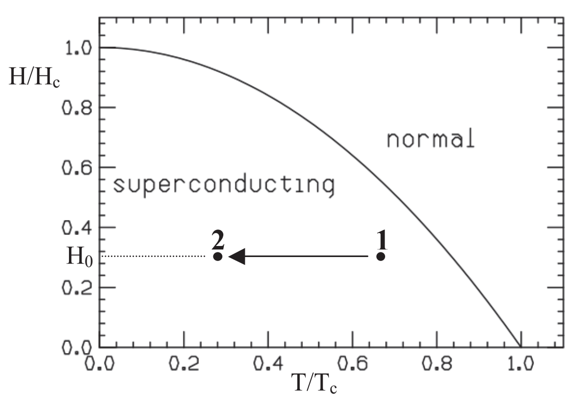

FIG. 1: Critical magnetic field versus temperature for a type I superconductor. We will consider the process where a system evolves from point 1 to point 2 along the direction of the arrow.

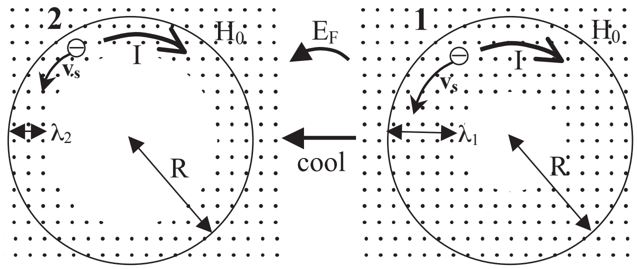

FIG. 2: Cylindrical superconductor seen from the top. The right (left) panel indicates the system in the state 1 (2) of Fig. 1. The dots indicate magnetic field H_0 coming out of the paper. The same current I flows in both states. The Faraday electric field E_F generated during the process points counterclockwise.

An azimuthal current circulates near its surface. From Ampere's law we have

$$\oint \vec{B} \cdot d\vec{\ell} = \frac{4\pi}{c} \int \vec{j}_s \cdot d\vec{S} = \frac{4\pi}{c} I \tag{1}$$

where $\vec{j}_s$ is the current density and I is the total current. Taking one side of the contour in the deep interior and the other one outside the cylinder we obtain

$$I = \frac{c}{4\pi} h H_0 \tag{2}$$

Assuming the current circulates within a layer of thickness λ_L of the surface, with current density j_s, the total current and current density are related by

$$I = j_s \lambda_L h \tag{3}$$

hence the current density is

$$j_s = \frac{c}{4\pi\lambda_L} H_0. \tag{4}$$

The London penetration depth varies with temperature, becoming smaller as the temperature decreases. From Eq. (4) we see that the supercurrent density increases as the temperature is lowered, but since it flows in an increasingly thinner layer the total current Eq. (2) is independent of temperature.

The current density is related to the superfluid density n_s and the superfluid velocity $\vec{v}_s$ by

$$\vec{j}_s = n_s e \vec{v}_s \tag{5}$$

with e the electron charge, and within London-BCS theory the superfluid velocity is given by [2]

$$\vec{v}_s = -\frac{e}{m_e c} \vec{A} \tag{6}$$

where $\vec{A}$ is the magnetic vector potential. For simplicity we ignore any difference between bare mass m_e and effective mass [3], this will not affect our results. From Eqs. (5) and (6)

$$\vec{j}_s = -\frac{n_s e^2}{m_e c} \vec{A} \tag{7}$$

so that

$$\vec{\nabla} \times \vec{j}_s = -\frac{n_s e^2}{m_e c} \vec{B} \tag{8}$$

with $\vec{B} = \vec{\nabla} \times \vec{A}$. From Ampere's law in differential form

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c} \vec{j}_s \tag{9}$$

taking the curl on both sides and using Eq. (8)

$$\nabla^2 \vec{B} = \frac{4\pi n_s e^2}{m_e c^2} \vec{B} = \frac{1}{\lambda_L^2} \vec{B}. \tag{10}$$

so that the magnetic field and the supercurrent decay to zero exponentially in the interior over distance λ_L, given in Eq. (10) as a function of superfluid density n_s. From Eq. (10)

$$n_s \lambda_L^2 = \frac{m_e c^2}{4\pi e^2}. \tag{11}$$

As the temperature is lowered, n_s increases and λ_L decreases keeping the product in Eq. (11) constant. BCS theory provides equations that give the temperature dependence of λ_L. The BCS prediction is very close to the behavior predicted by the two-fluid model [1]

$$\frac{1}{\lambda_L(T)^2} = \frac{1}{\lambda_L(0)^2}(1 - (\frac{T}{T_c})^4) \tag{12}$$

except at very low temperatures where BCS predicts exponential rather than power-law temperature dependence [2]. However we will not be interested in that regime, and will use Eq. (12) in this paper for simplicity.

From Eq. (6), using Stokes' theorem and the fact that the supercurrent flows in the surface layer of thickness λ_L we obtain for the magnitude of the superfluid velocity

$$v_s = -\frac{e\lambda_L}{m_e c} B \tag{13}$$

so the superfluid velocity decreases as the temperature is lowered and λ_L decreases. The magnitude of the current density in terms of the magnetic field is given by

$$j_s = \frac{n_s e^2}{m_e c} \lambda_L B = \frac{c}{4\pi\lambda_L} B. \tag{14}$$

We will also be interested in the mechanical angular momentum carried by the electrons in the supercurrent. The mechanical momentum density of electrons at position $\vec{r}$ is [4]

$$\vec{\mathcal{P}}(\vec{r}) = \frac{m_e}{e} \vec{j}_s(\vec{r}) \tag{15}$$

where $\vec{j}_s(\vec{r})$ is the current density at position $\vec{r}$. Assuming the supercurrent circulates on the surface layer of thickness λ_L and using Eqs. (5), (11) and (13) the total mechanical angular momentum of the electrons in the supercurrent is, assuming $\lambda_L << R$

$$\vec{L}_e = -\frac{m_e c}{2e} h R^2 H \hat{z} \tag{16}$$

so that the total electronic angular momentum does not change with temperature. Consequently we can conclude by momentum conservation that the body as a whole does not change its angular momentum when the system is cooled.

III. THE PROCESS AND THE QUESTIONS

We consider the process shown in Fig. 1, where a superconducting cylinder in a magnetic field is cooled from initial temperature T_1 to finite temperature T_2. The London penetration depth changes from $\lambda_L(T_1) \equiv \lambda_1$ to $\lambda_L(T_2) \equiv \lambda_2$, with $\lambda_2 < \lambda_1$.

During this process, magnetic field is expelled, since initially it penetrates up to radius $r_1 \sim R - \lambda_1$ and at the end only to radius $r_2 \sim R - \lambda_2$, as shown schematically in Fig. 2. In other words, the field was expelled from the region $R - \lambda_1 < r < R - \lambda_2$, a ring of thickness $\lambda_1 - \lambda_2$. This gives rise to a Faraday electric field E_F pointing in counterclockwise direction that is determined by Faraday's law,

$$\oint \vec{E}_F \cdot d\vec{\ell} = -\frac{1}{c}\frac{\partial}{\partial t} \int \vec{B} \cdot d\vec{S} \tag{17}$$

If the process occurs over a time t_0 Eq. (17) yields for the time integral of the Faraday field

$$\int_0^{t_0} E_F dt = \frac{H_0}{c}(\lambda_1 - \lambda_2) \tag{18}$$

The Faraday field acts on the superfluid electrons as

$$\frac{d}{dt}v_s = \frac{e}{m_e}E_F \tag{19}$$

and integrating both sides of Eq. (19) over time and using Eq. (18), the change in superfluid velocity is

$$\Delta v_s = \frac{e}{m_e}\int_0^{t_0} E_F dt = \frac{eH_0}{m_e c}(\lambda_1 - \lambda_2) = \frac{eH_0}{m_e c}\Delta\lambda_L \tag{20}$$

which is precisely what Eq. (13) predicts. So as the London penetration depth decreases from λ_1 to λ_2 the superfluid velocity decreases as given by Eq. (13), and the time variation of the superfluid velocity is completely accounted for by the action of the Faraday electric field on the superfluid carriers.

According to the above, the Faraday field, pointing in counterclockwise direction, will change the angular momentum of the superfluid electrons, increasing their momentum in clockwise direction. At the same time, it will impart counterclockwise angular momentum to the positive ions, i.e. to the body as a whole. However we have seen that the total electronic angular momentum L_e (Eq. (16)) doesn't change in this process, hence neither does the total ionic angular momentum. How is this possible?

The reason is, as the temperature is lowered and λ_L decreases the number of superfluid electrons $n_s(T)$ will increase, according to Eq. (11). In the process of normal electrons condensing into the superconducting state they have to acquire counterclockwise momentum, of exactly the right magnitude to cancel the clockwise momentum imparted on the superfluid electrons by the Faraday field. And the same process of condensation has to impart clockwise momentum to the body as a whole to counteract the counterclockwise momentum imparted to the body by the Faraday field.

The theory of superconductivity has to explain the physical mechanisms by which these changes in momenta happen in the process of normal electrons condensing into the superconducting state. To the best of our knowledge this has never been discussed in the superconductivity literature. In refs [5, 6] we argued that BCS-London theory does not have the physical elements necessary to explain these processes.

Furthermore, we have to remember that 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. Similarly within BCS theory there is the superfluid and Bogoliubov quasiparticles at finite temperature, we will call the latter 'normal electrons'. The Faraday electric field will impart clockwise momentum to these normal electrons, and this momentum will decay to zero through scattering with impurities or phonons. These are irreversible processes, that generate Joule heat and entropy. However, it should be possible to cool a thermodynamic system in a reversible way, without entropy generation.

In the following sections we analyze the dynamics and the thermodynamics of these processes in detail and conclude that they cannot be understood within the conventional theory of superconductivity, and for that reason the conventional theory is incompatible with the laws of physics.

IV. SOME CAVEATS

In our analysis of the process where the system evolves from its initial to its final state, we will assume for simplicity that the system is in approximate thermodynamic equilibrium at all times. Let us discuss what this means.

(1) We will assume that the temperature is approximately uniform over the entire system throughout the process. This requires the thermal conductivity of the system to be sufficiently large for a given rate of the process that any temperature gradients will disappear in a time much shorter than the duration of the entire process. Note that the thermal conductivity of a metal is expected to be proportional to its electrical conductivity (Wiedemann-Franz law). We will find that the Joule heat generated, that leads to a thermodynamic inconsistency, is proportional to the electrical conductivity. A larger electrical conductivity implies a larger thermal conductivity and hence a more rapid homogenization of the temperature field, therefore temperature inhomogeneities will not play a role precisely in the cases where the Joule heat generated is largest.

(2) At a given instant during the process, when the system is at temperature T, we will assume that the London penetration depth is given by its equilibrium value $\lambda_L(T)$. This is a reasonable assumption because we have in

mind processes where the temperature changes by a few degrees Kelvin with a rate of change slower than (degree Kelvin/millisecond); instead the time scale associated with the process of normal-superfluid conversion is expected to be much faster, of order 10^{-8} s or smaller [7–10], and scattering times of normal electrons should be of order $10^{-10}s$ or smaller. Under these circumstances the magnetic field and current configuration at a given instant t will be given accurately by the equilibrium values corresponding to temperature $T(t)$ and London penetration depth $\lambda_L(T(t))$.

Furthermore, we will assume in our treatment that the thermodynamics of the superfluid and Bogoliubov quasiparticle excitations can be described by a two fluid model, i.e. superfluid and normal fluid in proportions that vary with temperature as given by that model [11, 12]. We will also assume for simplicity that the London-penetration depth dependence on temperature is given by the two-fluid model, and that the scattering time for conduction of normal fluid in the superconducting state is the same as in the normal state. These are clearly reasonable assumptions, any quantitative inaccuracy associated with them will not affect our conclusions which are of a qualitative nature.

Note that the crucial assumption that the normal component in the superconducting state will dissipate Joule heat in the presence of an electric field follows from the conventional theory of superconductivity, as discussed by Tinkham [13]. In particular, Tinkham explains in Chapter 2: *"According to the first London equation, a time-varying supercurrent requires an electric field E to accelerate and decelerate the superconducting electrons. This electric field also acts on the so-called "normal" electrons (really thermal excitations from the superconducting ground state, as we shall see in Chap. 3), which scatter from impurities, and can be described by Ohm's law. In this section, we introduce the so-called two-fluid model, which describes the electrodynamics that results from the superposition of the response of the "superconducting" and "normal" electron fluids to alternating electromagnetic fields. Although this model is, of course, an oversimplification, it is the standard working approximation for understanding electrical losses in superconductors, so that dissipation can be anticipated and minimized in applications such as microwave resonators. The validity of the model is restricted, however, to frequencies below the energy gap frequency, since above that frequency additional loss mechanisms set in and the dissipation approaches that in the normal state."* The process we are considering in this paper corresponds to 'frequencies below the energy gap frequency' so we don't expect additional loss mechanisms to set in.

V. EXACT EQUILIBRIUM EQUATIONS FOR THE CYLINDER

We recall briefly the exact solution of the equilibrium electrodynamic equations for an infinite cylinder [14]. Equation (10) for the magnetic field $\vec{B}$ is, in cylindrical coordinates

$$\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial B(r)}{\partial r}) - \frac{1}{\lambda_L^2}B(r) = 0 \tag{21}$$

assuming cylindrical symmetry. From Eq. (9), the current is given by

$$\vec{j}_s(r) = -\frac{c}{4\pi}\frac{\partial B}{\partial r}\hat{\theta} \tag{22}$$

With boundary condition $B(R) = H_0$ the solution is

$$B(r) = H_0\frac{J_0(ir/\lambda_L)}{J_0(iR/\lambda_L)} \tag{23a}$$

$$j_s(r) = \frac{c}{4\pi\lambda_L}H_0 i\frac{J_1(ir/\lambda_L)}{J_0(iR/\lambda_L)} \tag{23b}$$

where J_0 and J_1 are Bessel functions, related by $J_1(x) = -(\partial/\partial x)J_0(x)$. They are given by the series expansions

$$J_0(x) = \sum_{m=0}^{\infty}(-1)^m\frac{(\frac{1}{2}x)^{2m}}{(m!)^2} \tag{24a}$$

$$J_1(x) = \sum_{m=0}^{\infty}(-1)^m\frac{(\frac{1}{2}x)^{2m+1}}{(m!)(m+1)!} \tag{24b}$$

and for large imaginary argument by

$$J_0(ix) = \frac{e^x}{\sqrt{x}} \tag{25a}$$

$$J_1(ix) = i\frac{e^x}{\sqrt{x}}. \tag{25b}$$

In the following we assume $R >> \lambda_L$ and consider all quantities derived from these equations to lowest order in (λ_L/R) only, for simplicity. We don't think this affects our reasoning and conclusions. In any event, it is straightforward to extend the treatment to avoid this approximation.

VI. EQUATIONS FOR LARGE R/λ_L

We consider a process where the temperature changes gradually so the system is always in equilibrium, between an initial time $t = 0$ and a final time $t = t_0$. The London penetration depth is given by $\lambda_L(t)$, with $\lambda_L(0) = \lambda_1$, $\lambda_L(t_0) = \lambda_2$. The magnetic field is given by

$$\vec{B}(r,t) = H_0 e^{(r-R)/\lambda_L(t)}\hat{z} \tag{26}$$

the magnetic vector potential by

$$\vec{A}(r,t) = H_0\lambda_L(t)e^{(r-R)/\lambda_L(t)}\hat{\theta} \tag{27}$$

the Faraday electric field by

$$\begin{aligned}\vec{E}(r,t) &= -\frac{1}{c}\frac{\partial A(r,t)}{\partial t} \\ &= -\frac{H_0}{c}(1+\frac{R-r}{\lambda_L})e^{(r-R)/\lambda_L(t)}\frac{\partial \lambda_L}{\partial t}\hat{\theta}\end{aligned} \tag{28}$$

the current density by

$$\vec{j}_s(r,t) = -\frac{c}{4\pi\lambda_L}H_0 e^{(r-R)/\lambda_L(t)}\hat{\theta} \tag{29}$$

the superfluid velocity by

$$\vec{v}_s(r,t) = -\frac{eH_0}{m_e c}\lambda_L(t)e^{(r-R)/\lambda_L(t)}\hat{\theta} \tag{30}$$

and the London penetration depth and superfluid density satisfy

$$n_s(t)\lambda_L(t)^2 = \frac{m_e c^2}{4\pi e^2}. \tag{31}$$

Eq. (29) for the supercurrent follows from Eq. (26) using Ampere's law, i.e. Ampere-Maxwell's law ignoring the Maxwell displacement current. This is justified because the ratio of the Maxwell term to the Ampere term is of order $(\partial\lambda_L/\partial t)^2/c^2$, which is utterly negligible compared to 1.

Note that, from Eqs. (28) and (30)

$$\frac{d\vec{v}_s(r,t)}{dt} = \frac{e}{m_e}\vec{E}(r,t), \tag{32}$$

in other words, the Faraday electric field causes the superfluid velocity to change (slow down) according to Newton's law, as one would expect.

The total electronic angular momentum at time t due to superfluid electrons only is given by (we omit time dependence for brevity)

$$\vec{L}_e^s(t) = hn_s\int d^2r m_e v_s(r)r = 2\pi hn_s m_e\int_0^R dr r^2 v_s(r) \tag{33}$$

and we know from Eq. (16) that $dL_e/dt = 0$, i.e. it is a constant of motion. We can write

$$\frac{dL_e}{dt} = \frac{dL_e^{(1)}}{dt} + \frac{dL_e^{(2)}}{dt} \tag{34}$$

with

$$\begin{aligned} \frac{dL_e^{(1)}}{dt} &= 2\pi h n_s \int_0^R dr r^2 m_e \frac{dv_s(r)}{dt} \\ &= 2\pi h n_s \int_0^R dr r^2 eE(r,t) \end{aligned} \tag{35}$$

where we used Eq. (32). This term has negative sign and expresses the fact that the Faraday electric field decreases the angular momentum of electrons in the supercurrent in the process where the temperature is lowered and the London penetration depth decreases. This is because the Faraday field wants to restore the magnetic field in the interior that is being pushed further out in this process, by reducing the supercurrent. But we know from Eq. (2) that the total supercurrent I doesn't change.

The second term in Eq. (34) then has positive sign, it increases the electronic angular momentum. It is given by (to lowest order in λ_L/R)

$$\frac{dL_e^{(2)}}{dt} = \frac{\partial n_s}{\partial t}[2\pi R\lambda_L h]m_e v_s(R)R. \tag{36}$$

The term in square brackets is the volume of the surface layer of thickness λ_L . What Eq. (36) says is that as electrons that are near the surface condense from the normal into the superconducting state, they 'spontaneously' acquire the speed $v_s(r)$ and the electronic angular momentum changes accordingly. Of course electrons in the interior also condense, but because they don't carry current they don't contribute to the change in angular momentum.

Associated with these electronic angular momentum changes there are also corresponding changes in the angular momentum of the ions, i.e. the body as a whole,

$$\frac{dL_i}{dt} = \frac{dL_i^{(1)}}{dt} + \frac{dL_i^{(2)}}{dt} = 0 \tag{37}$$

with

$$\frac{dL_i^{(1)}}{dt} = -\frac{dL_e^{(1)}}{dt} \tag{38a}$$

$$\frac{dL_i^{(2)}}{dt} = -\frac{dL_e^{(2)}}{dt}. \tag{38b}$$

The first one, Eq. (38a), is easily understood. Just like the Faraday electric field transfers clockwise momentum to the electrons, it transfers equal in magnitude and opposite in direction (i.e. counterclockwise) momentum to the positive ions. The second one, Eq. (38b), is clockwise momentum transferred to the body when normal electrons near the surface condense into the superconducting state.

The theoretical explanation of these processes has to explain the physical mechanism(s) that cause(s) normal electrons to change their angular momentum when they condense into the superconducting state, Eq. (36), and at the same time cause(s) the body to acquire the same angular momentum in opposite direction. These questions have not yet been discussed in the literature on conventional superconductivity. We hope this will be done soon. We don't believe it is possible to understand these processes within the conventional theory [5, 6].

VII. NORMAL CURRENT AND JOULE HEAT

As discussed in Sect. IV, within London theory we can think of the superconductor as a two-fluid model, a mixture of normal fluid and superfluid, with proportions that vary with temperature. The same is true within BCS theory, where the normal fluid is composed of Bogoliubov quasiparticles. The normal fluid will be subject to normal scattering processes [13]. In the presence of an electric field, a normal current will be generated, and dissipation will occur.

The normal current flowing in counterclockwise direction induced by the electric field is given by

$$\vec{j}_n(r,t) = \sigma_n(t)\vec{E}(r,t) \tag{39}$$

with σ_n the normal conductivity, which we can write as

$$\sigma_n(t) = \frac{n_n(t)e^2}{m_e}\tau \tag{40}$$

where τ is the Drude scattering time and where the normal electron density is given by

$$n_n(t) = n - n_s(t) \tag{41}$$

with $n_s(t)$ given by Eq. (31), and n the superfluid density at zero temperature, given by

$$n\lambda_L^2(T=0) = \frac{m_e c^2}{4\pi e^2}. \tag{42}$$

The power dissipated per unit volume is

$$\frac{\partial w}{\partial t} = \sigma_n(t)E(r,t)^2 \tag{43}$$

with the electric field given by Eq. (28). Integrating Eq. (43) over the volume of the cylinder we find for the Joule heat dissipated per unit time

$$\frac{\partial W}{\partial t} \equiv \int d^3r \frac{\partial w}{\partial t} = \sigma_n \frac{H_0^2}{c^2}(\frac{\partial \lambda_L}{\partial t})^2 \frac{\pi h R \lambda_L(t)}{2} \tag{44}$$

We can write the normal state conductivity in the form

$$\sigma_n(t) = \frac{n_n(t)}{n_s(t)}\frac{1}{\lambda_L(t)^2}\frac{c^2}{4\pi}\tau = (1 - \frac{\lambda_L(0)^2}{\lambda_L(t)^2})\frac{1}{\lambda_L(0)^2}\frac{c^2}{4\pi}\tau \tag{45}$$

so Eq. (44) is

$$\frac{\partial W}{\partial t} = \frac{H_0^2}{8\pi}(\frac{1}{\lambda_L(0)^2} - \frac{1}{\lambda_L(t)^2})(\frac{\partial \lambda_L}{\partial t})^2(\pi h R \lambda_L(t))\tau. \tag{46}$$

Note that the total Joule heat dissipated, i.e. the time integral of Eq. (46), will depend on the speed of the process. For example, if we assume that $\partial\lambda_L/\partial t$ is time-independent, we have

$$\int_0^\infty \frac{\partial W}{\partial t} dt = (\frac{\partial \lambda_L}{\partial t}) \int_{\lambda_1}^{\lambda_2} d\lambda \frac{H_0^2}{8\pi}(\frac{1}{\lambda_L(0)^2} - \frac{1}{\lambda^2})(\pi h R \lambda)\tau \tag{47}$$

so the total Joule heat generated is proportional to the rate of change of the London penetration depth with time.

Near the critical temperature, the London penetration depth varies extremely rapidly with temperature and it is clear that Eq. (46) can become very large. Since in the laboratory it is simpler to control the change in temperature with time rather than the London penetration depth, let us rewrite Eq. (46) in terms of the former assuming for simplicity the relation derived from the two-fluid model

$$\frac{1}{\lambda_L(t)^2} = \frac{1}{\lambda_L(0)^2}(1 - (\frac{T(t)}{T_c})^4) \tag{48}$$

so we can write, in terms of $T = T(t)$,

$$(\frac{\partial \lambda_L}{\partial t})^2 = 4(\frac{T}{T_c})^6 \frac{\lambda_L(0)^2}{[1-(\frac{T}{T_c})^4]^3}\frac{1}{T_c^2}(\frac{\partial T}{\partial t})^2 \tag{49}$$

and Eq. (46) is

$$\begin{aligned}\frac{\partial W}{\partial t} &= \frac{H_0^2}{8\pi}(\frac{T}{T_c})^{10} \\ &\times \frac{1}{[1-(\frac{T}{T_c})^4]^{7/2}}\frac{1}{T_c^2}(\frac{\partial T}{\partial t})^2(4\pi h R \lambda_L(0))\tau.\end{aligned} \tag{50}$$

Equation (50) says that if we cool a superconductor below T_c at any reasonable cooling rate, the amount of Joule heat dissipated will be arbitrarily large provided we start the cooling process sufficiently close to T_c. The same will be true if we heat a superconductor below T_c to a temperature very close to T_c.

However we also need to consider that in a finite magnetic field H_0, the divergence in the London penetration depth as T approaches T_c will be cut off because the system will undergo a first order transition to the normal state. Nevertheless, the problem persists. Let us assume for simplicity the two-fluid model expression for the critical magnetic field as function of temperature

$$H_0 = H_c(1-(\frac{T_1}{T_c})^2) \tag{51}$$

where H_c is the zero temperature critical field, and T_1 is a temperature close to T_c:

$$\frac{T_1}{T_c} = 1-\delta_1 \tag{52}$$

with δ_1 small. For the system at temperature T below T_1, given by

$$\frac{T}{T_c} = 1-\delta_1-\delta_2 \tag{53}$$

we have for Eq. (50)

$$\begin{aligned} \frac{\partial W}{\partial t} &= \frac{H_c^2}{8\pi}(\frac{T}{T_c})^{10} \\ &\times \frac{1}{8\delta_1^{3/2}(1+\delta_2/\delta_1)^{7/2}}\frac{1}{T_c^2}(\frac{\partial T}{\partial t})^2(4\pi hR\lambda_L(0))\tau. \end{aligned} \tag{54}$$

which becomes arbitrarily large for sufficiently small values of δ_1, δ_2.

The reader may argue that the divergence that we are pointing out is not really a problem. First, because of the smallness of τ, for any realistic values of $\partial T/\partial t$ Eq. (54) will be extremely small unless we are extremely close to T_c. The reader may argue that in that unrealistic regime some other physics may come in, involving fluctuations, that invalidates our simple treatment.

However, we argue that the Joule-heat dissipation pointed out here brings other fundamental problems beyond the quantitative divergence pointed out above. Superconductors are supposed to be governed by conventional thermodynamics, and it should be possible to describe *reversible* cooling and heating in the superconducting state. The generation of normal current due to the Faraday field and associated dissipation makes this impossible. In the next sections we show explicitly that thermodynamics is violated.

VIII. MORE NORMAL CURRENT

There is in fact another contribution to the normal current besides the one given by Eq. (39) according to the conventional theory.

As the temperature decreases the superfluid density increases, by additional normal electrons joining the superfluid. Condensing normal electrons 'spontaneously' acquire the velocity of electrons in the supercurrent, thus increasing the electronic momentum in counterclockwise direction according to Eq. (36). Conservation of momentum requires that the ions acquire equal momentum in opposite direction, i.e. clockwise, Eq. (38b). How does that happen?

According to the conventional theory, as normal electrons condense a clockwise momentum imbalance is created in the normal region [6, 17], which is transferred to the body by normal collisions. This momentum imbalance corresponds to a *counterclockwise* normal current that adds to the one induced by the Faraday field considered in Sect. VI. So the Joule heat generated will be even larger than computed in Sect. VI.

Quantitatively, the change in superfluid density for a given change in penetration depth is, from Eq. (11)

$$\Delta n_s = -2n_s\lambda_L\Delta\lambda_L \tag{55}$$

and the change in normal electron density is $\Delta n_n = -\Delta n_s$. In a time interval τ, the normal collision time, the normal electron density then changes by

$$\Delta n_n = 2n_s\lambda_L\frac{\partial\lambda_L}{\partial t}\tau \tag{56}$$

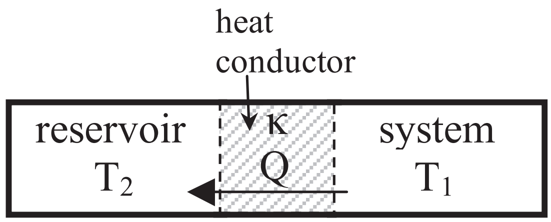

FIG. 3: The system (superconductor in a magnetic field) at initial temperature T_1 is connected to a heat reservoir at temperature $T_2 < T_1$ through a heat conductor of thermal conductivity κ. The entire assembly is thermally and mechanically insulated from its environment.

The change in normal electron momentum density in that time interval is

$$\Delta\mathcal{P} = \Delta n_n m_e v_s \tag{57}$$

since each condensing normal electron aquired velocity v_s, and the resulting normal current density is

$$j'_n(r,t) = \frac{e}{m_e}\Delta\mathcal{P} = 2\frac{n_s e^2}{m_e}\tau\frac{H_0}{c}e^{(r-R)/\lambda_L}\frac{\partial\lambda_L}{\partial t} \tag{58}$$

where we used Eq. (30) for v_s. The Joule heat dissipated per unit time due to this current in the presence of the electric field $E(r,t)$, Eq. (28), is

$$\frac{\partial W'}{\partial t} = \int d^3r j'_n(r,t)E(r,t) \tag{59}$$

and yields

$$\frac{\partial W'}{\partial t} = 2\frac{n_s}{n_n}\sigma_n\frac{H_0^2}{c^2}(\frac{\partial\lambda_L}{\partial t})^2\frac{\pi hR\lambda_L(t)}{2} \tag{60}$$

and added to Eq. (44) yields for the total Joule heat per unit time

$$\frac{\partial W_{total}}{\partial t} = [1 + 2\frac{n_s(t)}{n_n(t)}]\frac{\partial W}{\partial t} \tag{61}$$

where $\partial W/\partial t$ was calculated in the previous section. So this new term is larger than the one calculated in the previous section at low temperatures, and smaller at high temperatures. In the two-fluid model, the crossover point is at $T = 0.904T_c$. So we conclude that over most of the temperature range below T_c, the Joule heat due to the normal current generated in the condensation process dominates over the one due to the normal current induced by the Faraday field.

IX. THERMODYNAMIC INCONSISTENCY

Irrespective of how the normal current originated, we argue that its presence and the resulting Joule heat is in contradiction with thermodynamics.

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 $\lambda_L(T_1)$.

We put it in thermal contact with a heat reservoir at temperature $T_2 < T_1$ through a thermal conductor 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.

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

$$Q = \int_{T_2}^{T_1} dTC(T) \tag{62}$$

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

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} dT \frac{C(T)}{T} \tag{63}$$

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

$$\Delta S_{univ} = \frac{Q}{T_2} + \Delta S \tag{64}$$

and is of course positive since we are dealing with an irreversible process, heat conduction between systems at different temperatures.

The Joule heat generated in this process can be calculated from time integration of Eq. (61)

$$\begin{aligned} Q_J &= \int_0^\infty dt \frac{\partial W_{total}}{\partial t} = \frac{H_0^2}{8\pi} \int_0^\infty dt (1 + 2\frac{n_s(t)}{n_n(t)}) \\ &\times (1 - \frac{\lambda_L(0)^2}{\lambda_L(t)^2}) \frac{1}{\lambda_L(0)^2} (\frac{\partial \lambda_L}{\partial t})^2 (\pi h R \lambda_L(t)) \tau. \end{aligned} \tag{65}$$

In addition, the Joule heat will generate entropy, given by

$$S_J = \int_0^\infty dt \frac{\partial W_{total}}{\partial t} \frac{1}{T(t)}. \tag{66}$$

It is clear that the magnitudes of Q_J and S_J will depend on how fast the system is evolving from the initial to the final state, being larger for larger $\partial\lambda_L/\partial t$, which in turn will depend on the thermal conductivity of the heat conductor, κ, that connects the system with the heat reservoir. If κ is extremely low, essentially no Joule heat will be generated nor Joule entropy. If κ is not extremely low, these quantities will not be negligible.

However, this does not make sense. Our system and the heat reservoir constitute our universe, their energy and entropy are functions of state, and the initial and final states in our process for both the system and the reservoir are uniquely defined. Therefore the heat transferred Q and the change in entropy of the universe ΔS_{univ} are uniquely defined by Eqs. (62)-(64). There is no room for either Q_J nor S_J. But within the conventional theory of superconductivity, a normal current is necessarily generated when the temperature changes below T_c, and nonzero Joule heat and Joule entropy are necessarily generated, unless the process happens infinitely slowly.

It is important to emphasize that this argument does not depend on the reservoir being infinite so that its temperature T_2 is unchanged, as assumed above for simplicity. For a finite 'reservoir', it and the system will reach an equilibrium temperature T_3, with $T_2 < T_3 < T_1$. If for a different cooling rate and different Joule heat generated the final equilibrium temperature were to be $T_4 \neq T_3$, it would imply that either the system or the 'reservoir' have negative heat capacity which is of course impossible. Because the system and the 'reservoir' constitute our 'universe', their final equilibrium temperature and their final states are uniquely defined, and the considerations given above apply.

To resolve this inconsistency without violating well established laws of electromagnetism and thermodynamics, we would have to conclude that the process happens infinitely slowly in nature, independent of the experimental conditions, e.g. the value of κ in Fig. 3. That is contradicted by experiment. Alternatively, we would have to conclude that the final state of the superconductor is not unique, but depends on how the state was reached, i.e. fast or slowly. This would be a return to the pre-1933 view of superconductors. Since Gorter's and Casimir's work in 1934 [1], continuing with London's work and BCS, the premise that in a simply connected superconductor the state of the system for a given external magnetic field is unique has been an essential component of our understanding of superconductivity. Unless we want to abandon that cherished concept, we have to conclude that the conventional theory is internally inconsistent, hence needs to be repaired or replaced.

X. THERMODYNAMICS OF THE PHASE TRANSITION

In this section we consider a somewhat related problem, concerning the thermodynamics of the normal-superconductor transition. We have considered some aspects of it already in previous work, ref. [6]. We will show here that the generation of Joule heat *does not* lead to difficulties in that case, in contrast to the situation considered in the previous section. In the following section we explain the reason for the difference in the two situations.

Let us denote by $H_c(T)$ the critical field at temperature T where normal and superconducting phases can coexist. Consider the three possible states shown in Fig. 4. In state 1, the system is in the normal state at temperature

$T+\Delta T$. In state 2, it is in the superconducting state at temperature $T+\Delta T$, in state 3 it is in the superconducting state at temperature T. The critical field at temperature T is denoted by $H_c \equiv H_c(T)$, at temperature $T+\Delta T$ the critical field is $H_c(1-p) \equiv H_c(T+\Delta T)$.

We consider the two possible routes for the transition shown in Fig. 5, in an applied magnetic field $H_c(T+\Delta T) = H_c(1-p)$. In route A, the system undergoes the N-S transition while on the coexistence curve, at temperature $T+\Delta T$. The transition proceeds infinitely slowly and no Joule heat is generated. After the system reaches the superconducting state, heat flows to the reservoir and the system cools to temperature T. In route B, the system in the normal state cools to temperature T first, and then makes the transition to the superconducting state. Let us call $L(T)$ the latent heat for our system, i.e. the heat transferred out of the system when it goes from normal to superconducting at temperature T.

A. Route A

The transition proceeds infinitely slowly, since the system is on the coexistence curve (state 1 to state 2 in Fig. 4). Therefore, no Joule heat is generated. The total heat transferred from the system to the heat reservoir between initial and final states is

$$Q_A = L(T+\Delta T) + C_s \Delta T \tag{67}$$

to first order in ΔT. We ignore the small change in C_s, the heat capacity in the superconducting state, as the temperature changes between $T+\Delta T$ and T, because it is a second order contribution.

The latent heat is transferred between the system at temperature $T+\Delta T$ and the reservoir at temperature T. The change in the entropy of the universe in this process is then

$$\begin{aligned} \Delta S_{univ,A} &= L(T+\Delta T)\left(\frac{1}{T} - \frac{1}{T+\Delta T}\right) \\ &+ O((\Delta T)^2) = \frac{L(T)}{T}\frac{\Delta T}{T} + O((\Delta T)^2). \end{aligned} \tag{68}$$

The heat transfer during the process of temperature equalization generates no entropy to this order.

B. Route B

Route B is slightly more complicated. The system is cooled to temperature T while still in the normal state, i.e. it is supercooled. Then it becomes superconducting by expelling the applied magnetic field $H_c(1-p)$, which is smaller than the coexistence field $H_c = H_c(T)$ ($p > 0$). This takes a finite amount of time and generates Joule heat, because the changing magnetic flux in the normal region generates a Faraday field and a normal current. The total heat transferred to the heat reservoir here is

$$Q_B = C_n \Delta T + L(T) + Q_J \tag{69}$$

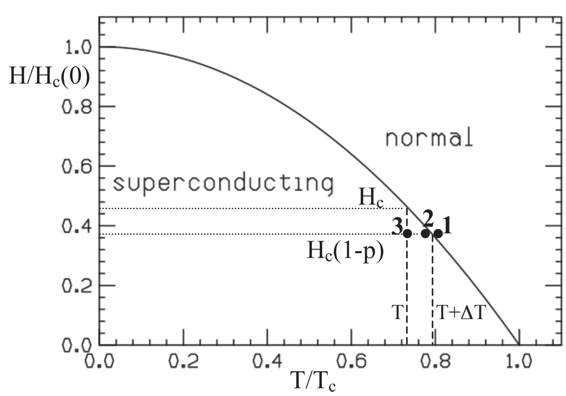

FIG. 4: In the figure, state 1 corresponds to the normal state at the coexistence line and state 2 to the superconducting state at the coexistence line. State 3 is a state at a slightly lower temperature.

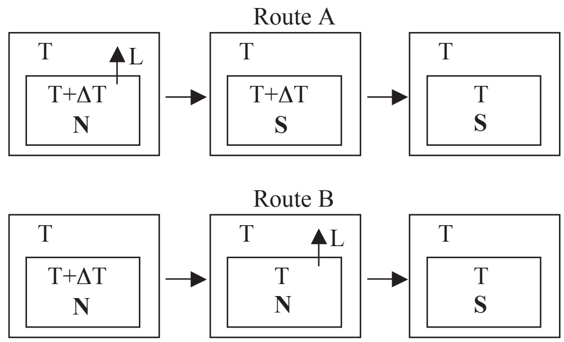

FIG. 5: Two routes for normal-superconductor (N-S) transition in an applied magnetic field $H_c(T+\Delta T)$ for a system initially at temperature $T+\Delta T$ that is put in thermal contact with a heat reservoir at temperature T. In route A, the system undergoes the transition to the superconducting state while at $T+\Delta T$, then cools. In route B, the normal system is cooled to temperature T, then it undergoes the transition to the superconducting state. L is the latent heat.

where Q_J is the Joule heat. The change in entropy of the universe in this process is

$$\Delta S_{univ,B} = O((\Delta T)^2) + 0 + \frac{Q_J}{T}. \tag{70}$$

In this equation, the first term corresponds to cooling in the normal state, which gives a second order contribution to the entropy; the second term is the change in the entropy of the universe when the latent heat and the Joule heat are transferred between the system and the environment at the same temperature T, hence it is zero. The third term, entropy generated by the production of Joule heat, accounts for the entire entropy generation to lowest order in ΔT in this process.

Now the initial and final states are the same in both routes. Therefore we *must have*:

$$\Delta S_{univ,B} = \Delta S_{univ,A} \tag{71a}$$

$$Q_B = Q_A \tag{71b}$$

Is that so?

For Eq. (71a) to be valid, we need, from Eqs. (68) and (70)

$$Q_J = \frac{L(T)}{T}\Delta T \tag{72}$$

and for Eq. (71b) to be valid we need, from Eqs. (67) and (69)

$$C_n\Delta T + L(T) + Q_J = L(T+\Delta T) + C_s\Delta T. \tag{73}$$

Assuming Eq. (72) does hold, Eq. (73) is to lowest order in ΔT

$$C_s - C_n = -\frac{\partial L(T)}{\partial T} + \frac{L(T)}{T}. \tag{74}$$

Now the Clausius-Clapeyron equation for a system with thermodynamic variables T, V, P (V=volume, P=pressure) undergoing a first order phase transformation is well known:

$$\frac{dP}{dT} = \frac{L(T)}{T\Delta V} \tag{75}$$

where L is the latent heat and ΔV the volume change. The analogous equation for a superconductor is [15]

$$\frac{dH_c}{dT} = \frac{L(T)}{T(M_s - M_n)} \tag{76}$$

where $M_n = 0$ is the magnetization in the normal state and $M_s = -H_c/(4\pi)$ is the magnetization in the superconducting state, from which it follows that

$$\frac{L(T)}{T} = -\frac{H_c}{4\pi}\frac{dH_c}{dT} \tag{77}$$

Replacing Eq. (77) in Eq. (74) we find

$$C_s - C_n = \frac{T}{4\pi}[(\frac{\partial H_c}{\partial T})^2 + H_c\frac{\partial^2 H_c}{\partial T^2}] \tag{78}$$

which is a well known relation, it follows from the formula

$$S_n(T) - S_s(T) = \frac{L(T)}{T} \tag{79}$$

for the entropy difference, and $C_a = T(\partial S_a/\partial T)$ with $a = s$ or n. At T_c, the second term on the right-hand side of Eq. (78) is zero, and Eq. (78) reduces to the even better known Rutgers relation for the specific heat jump at T_c.

Finally, we need to prove that the Joule heat dissipated in route B is indeed given by Eq. (72). The calculation is similar to the one we did in ref. [6] for the reverse process, the superconductor-normal transition. We discuss it in Appendix A, where we show that

$$Q_J = \frac{H_c^2}{4\pi}p. \tag{80}$$

From $H_c(T + \Delta T) = H_c(T)(1 - p)$ we have

$$p = -\frac{1}{H_c}\frac{\partial H_c}{\partial T}\Delta T \tag{81}$$

hence from Eqs. (80) and (81) and using Eq. (77)

$$Q_J = -\frac{H_c}{4\pi}\frac{\partial H_c}{\partial T} = \frac{L(T)}{T} \tag{82}$$

in agreement with Eq. (72).

This also implies that there is no further entropy generation in the process of transferring momentum to the body in the process of normal-superfluid conversion. However, we showed in Ref. [6] that within the conventional theory this would not be possible: the process generates a momentum imbalance in the normal electron distribution [17] that can only be resolved by transferring momentum to the body by normal scattering, thus generating additional Joule heat [6]. Therefore, already in Ref. [6] we had concluded that the conventional theory violates the laws of thermodynamics.

The two routes that we have considered here, A and B, correspond to having the situations in Fig. 3 where (A) $\kappa \to 0$ and (B) $\kappa \to \infty$, i.e. heat being transferred from the system to the reservoir infinitely slowly and infinitely fast. Since we get the same result in the two limits, one without Joule heat, one with Joule heat, it is reasonable to assume we would get the same result for any value of κ and intermediate values for Joule heat. No inconsistency here.

XI. SIMILARITIES AND DIFFERENCES BETWEEN THE PROCESSES IN SECTS. VIII AND IX

In both Sect. IX and Sect. X we have considered processes where a magnetic field is expelled from the interior of a superconductor, which according to Maxwell's electromagnetism generates a Faraday electric field. In both Sects. IX and X we have made the usual assumption that normal electrons respond to an electric field by generating a normal current, that undergoes normal scattering processes and generates Joule heat. Yet we have reached very different conclusions, namely that Sect. X satisfies thermodynamics and Sect. IX violates it. Let us compare the two situations.

An important difference is that in Sect. X there is a natural mechanism that determines the speed at which the transition occurs in route B, first elucidated by Pippard [18]: as the magnetic field $H_c(1 - p)$ is expelled at temperature T, the induced normal current generates a magnetic field in the same direction as the applied one, that increases the magnetic field at the phase boundary to exactly $H_c = H_c(T)$. The transition cannot proceed faster because that would make the normal current larger and the magnetic field at the phase boundary larger than H_c, reversing the direction of phase boundary motion. It will also not proceed slower because microscopic times governing the normal-superconductor transition are obviously very fast, and it is energetically favorable for the system to go superconducting as fast as it can. Therefore, the magnitude of p sets the rate at which the transition will take place, and hence the amount of Joule heat that will be generated. There is no wiggle room.

In contrast, there is no similar mechanism in Sect. IX to limit the speed of the transition. First, we can assume that the entire process occurs at temperatures $T << T(H_0)$, with $H_0 = H_c(T)$, in other words, far from the coexistence curve (see Fig. 1). Therefore, the magnetic field generated by the normal current will not increase the magnetic field above the critical field at that temperature, in contrast to the situation in Sect. X. More importantly, in Sect. IX the magnetic field generated by the normal current will immediately induce (through the Faraday field created by it) a counter-supercurrent that will keep the magnetic field in the deep interior zero at all times. Therefore, there does not appear to be any constraint on what the rate of the transition can be in Sect. IX, other than the thermal conductivity of the heat conductor between the system and the reservoir. This leads to the absurd conclusion that in the limit where the heat conductor has arbitrarily large thermal conductivity the Joule heat generated becomes arbitrarily large. But there is no source of energy to generate such Joule heat.

The essential difference between the situations in Sects. IX and X is that in Sect. X the normal current was induced in the normal region, and in Sect. IX it was induced in the superconducting region. As a matter of fact, we showed in ref. [6] that the Joule heat Eq. (80) generated during the transition results from action of the electric field *in the normal region only* (Eqs. 29) to (36) of [6]). In other words, even if not explicitly stated in ref. [6], we implicitly assumed, without justifying it, that there was no Joule heat generated in the superconducting region within λ_L of the phase boundary during the transition, even though an electric field does exist in that region. If we had included such contribution, we would have obtained a correction to Eq. (80) that would have spoiled the agreement with thermodynamics. In light of this it is not surprising that we find disagreement with thermodynamics in Sect. IX, where the Faraday field acts only in the superconducting region since there is no normal region.

The bottom line is: in order to get agreement with thermodynamics it is necessary to assume that an electric field does not induce a normal current in a superconductor at finite temperatures, where normal electrons and superfluid electrons coexist, when the temperature changes. This is contrary to what the conventional theory of superconductivity predicts.

XII. ELECTROMAGNETIC ENERGY

It is interesting to analyze the allocation of electromagnetic energy in the process we are considering. According to Poynting's theorem (also used in Appendix A),

$$\frac{\partial}{\partial t}\left(\frac{B^2}{8\pi}\right) = -\vec{J}\cdot\vec{E} - \frac{c}{4\pi}\vec{\nabla}\cdot(\vec{E}\times\vec{B}) \tag{83}$$

where the left side is the change in electromagnetic energy density, the first term on the right side is minus the work done by the electromagnetic field on charges, and the second is minus the outflow of electromagnetic energy.

Let us first assume there is no normal current. So Eq. (83) is

$$\frac{\partial}{\partial t}\left(\frac{B^2}{8\pi}\right) = -\vec{j}_s\cdot\vec{E} - \frac{c}{4\pi}\vec{\nabla}\cdot(\vec{E}\times\vec{B}) \tag{84}$$

with $\vec{B}$, $\vec{E}$ and $\vec{j}_s$ given by eqs. (26), (28) and (29). The left side of Eq. (84) is

$$\frac{\partial}{\partial t}\left(\frac{B^2}{8\pi}\right) = \frac{H_0^2}{4\pi}\frac{R-r}{\lambda_L^2}e^{2(r-R)/\lambda_L}\frac{\partial\lambda_L}{\partial t} \tag{85}$$

and the terms on the right side,

$$-\vec{j}_s\cdot\vec{E} = -\frac{H_0^2}{4\pi\lambda_L}\left(1+\frac{R-r}{\lambda_L}\right)e^{2(r-R)/\lambda_L}\frac{\partial\lambda_L}{\partial t} \tag{86}$$

and

$$-\frac{c}{4\pi}\vec{\nabla}\cdot(\vec{E}\times\vec{B}) = \tag{87}$$

$$\frac{H_0^2}{4\pi}\frac{\partial}{\partial r}\left[\left(1+\frac{R-r}{\lambda_L}\right)e^{2(r-R)/\lambda_L}\right]\frac{\partial\lambda_L}{\partial t} \tag{88}$$

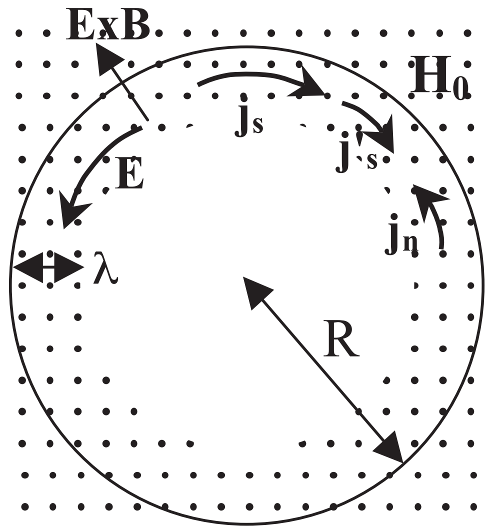

FIG. 6: Direction of electric field $\vec{E}$, supercurrents $\vec{j}_s$ and $\vec{j}'_s$, normal current $\vec{j}_n$ and Poynting vector (proportional to $\vec{E}\times\vec{B}$) in the process of *cooling* the superconductor.

and it is easily seen by substitution that Eq. (84) holds.

In Eq. (84), the left side is negative (recall that $\partial\lambda_L/\partial t$ is negative), since the magnetic energy is decreasing as we cool and magnetic field lines move out. The second term on the right is even more negative, more electromagnetic energy is flowing out than the decrease in magnetic energy in the interior. This is because the first term on the right is positive, the electric field decelerates the supercurrent, hence does negative work on the charges. In other words, the supercurrent is giving energy to the electromagnetic field, energy that it acquired in the process of normal electrons condensing into the superfluid.

Assume now there is also normal current. At first sight it may seem that Poynting's theorem will be violated if we substitute $\vec{j}_s$ by $\vec{j}_s+\vec{j}_n$ in Eq. (84). The reason it is not is that when there is normal current there is also an additional supercurrent, $\vec{j}'_s=-\vec{j}_n$. This new supercurrent is induced because the normal current creates a magnetic field, and in that process Faraday's law creates a magnetic field that induces this new supercurrent, which ensures that the magnetic field doesn't change, and in particular remains zero in the deep interior of the cylinder. So the energy balance equation is now

$$\frac{\partial}{\partial t}(\frac{B^2}{8\pi})=-(\vec{j}_s+\vec{j}'_s)\cdot\vec{E}-\vec{j}_n\cdot\vec{E}-\frac{c}{4\pi}\vec{\nabla}\cdot(\vec{E}\times\vec{B}) \tag{89}$$

with the same $\vec{B}$ and E as before. So Poynting's theorem continues to hold, but now there are two terms in Eq. (89) representing work done by the electromagnetic field on charges. The first term is positive and larger than before, since the supercurrent is larger, so the field is doing more negative work on the supercurrent than before. The second term is negative, representing the positive work that the field does on normal charges, since the normal current is in the same direction as the electric field, and that work is dissipated as Joule heat. Figure 6 shows the directions of currents, Faraday field and Poynting vector in the cooling process.

The faster the process goes, i.e. the larger the thermal conductivity κ of the heat conductor in Fig. 3 is, the larger will be j'_s, j_n, and the associated Joule heat Q_J and associated Joule entropy S_J. 'Somebody' has to supply the energy to create j'_s, that is transferred to j_n through the electromagnetic field and then converted into Joule heat. The only 'somebody' here is the superconductor.

As the superconductor cools, electrons condense into the superfluid and thereby lower their energy. Part of that energy difference is heat transferred to the reservoir, and part is transferred to the electromagnetic field via the first term on the right in Eq. (84). When the temperature decreases from T to $T-\Delta T$ we can write for these terms

$$\Delta E=\Delta Q+\Delta E_{em}. \tag{90}$$

Both ΔE and ΔQ are determined by the initial and final temperatures, T to $T-\Delta T$. In particular, $\Delta Q = T(\partial S/\partial T)\Delta T$. So ΔE_{em}, the energy transferred to the electromagnetic field, is fixed. It is given by the space and time integral of the second term in Eq. (84), which yields

$$\int_0^\infty dt\int d^3r(-\vec{j}_s\cdot\vec{E})=\frac{3}{8}H_0^2Rh[\lambda_L(T)-\lambda_L(T-\Delta T)] \tag{91}$$

and is independent of how fast or slow the cooling is. Therefore, there is no extra energy to create j_s', therefore it is not possible that j_n exists either.

XIII. MORE ON THERMODYNAMICS

We have argued that generation of Joule heat in a process where the temperature of the superconductor changes, always below T_c, leads to violation of both the first and second law of thermodynamics. In this section we consider the possibility that through some unknown mechanism conservation of energy can be maintained, and show that even in that case the second law would be violated.

Consider an intermediate step in the process, where the system changes its temperature from T to $T-\Delta T$. 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.

The total amount of heat transferred from the system to the reservoir has to be the same for (a) and (b), since the initial and final states of both the system and the electromagnetic field are the same, and hence also those of the reservoir. Let's call that heat ΔQ. For process (a), we have

$$\Delta Q = C(T)\Delta T \tag{92}$$

where $C(T)$ is the equilibrium heat capacity of the system. No Joule heat is generated.

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)

$$\Delta Q = C_r(T)\Delta T + \Delta Q_J \tag{93}$$

transferred from the system to the reservoir, the same as in process (a), respecting the first law. Both terms in Eq. (93) would depend on the speed of the process, the faster the process the smaller the first term and the larger the second term.

However, consider the change in entropy of the universe. The change in entropy of the reservoir in both processes is

$$\Delta S_{res} = \frac{\Delta Q}{T_2} \tag{94}$$

and the change in entropy of the system in both processes is (to lowest order in ΔT)

$$\Delta S_{sys} = -\frac{\Delta Q}{T} \tag{95}$$

In process (a) that is all there is, so the change in entropy of the universe is

$$\Delta S_{univ}^{(a)} = \Delta S_{res} + \Delta S_{sys} = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T} \tag{96}$$

which is of course larger than zero since $T > T_2$. In process (b), in addition to these, we need to take into account that generation of Joule heat generates entropy:

$$\Delta S_J = \frac{\Delta Q_J}{T}. \tag{97}$$

Therefore, the change in entropy of the universe in process (b) is

$$\Delta S_{univ}^{(b)} = \Delta S_{univ}^{(a)} + \Delta S_J > \Delta S_{univ}^{(a)}. \tag{98}$$

However, entropy is a function of state. Therefore, the second law of thermodynamics is violated by Eq. (98).

Finally, to try to get around this problem let us consider the possibility that the system lowers its entropy by a larger amount than Eq. (95) in the process of transferring heat to the reservoir in process (b). This would happen if the system is at a slightly lower temperature. Indeed one can argue that to generate the normal current the system has to supply energy, and that would lower its temperature from T to $T-\delta T$, where δT is determined by the equation

$$\Delta Q_J = C(T)\delta T. \tag{99}$$

The change in entropy of the system would then be, rather than Eq. (95)

$$\Delta S_{sys}^{(b)} = -\frac{\Delta Q}{T-\delta T} = -\frac{\Delta Q}{T} - \frac{\Delta Q}{T}\frac{\delta T}{T} \tag{100}$$

or, using Eqs. (99) and (92)

$$\Delta S_{sys}^{(b)} = -\frac{\Delta Q}{T} - \frac{\Delta Q_J}{T}\frac{\Delta T}{T} \tag{101}$$

so that the change in entropy of the universe in process (b) would be

$$\Delta S_{univ}^{(b)} = \Delta S_{univ}^{(a)} + \Delta S_J(1 - \frac{\Delta T}{T}) \tag{102}$$

and the violation of the second law of thermodynamics is not resolved.

XIV. AN ANALOGY

To understand the problems encountered with thermodynamics better we will consider an analogy here. Figure 7 shows schematically field lines for a superconductor of finite height in a uniform magnetic field. As the temperature is lowered from T_1 (left panel) to T_2 (right panel) the London penetration depth decreases and the magnetic field lines move outward. The initial and final states correspond to points 1 and 2 in the phase diagram of Fig. 1, and are the same no matter how fast or slow the process of cooling the superconductor is.

Imagine now that we place a small normal metal cylinder on top of our superconducting cylinder, as shown in Fig. 8, and we repeat the experiment. The final state will depend on the electrical conductivity of the normal metal and the speed at which the transition occurs. In particular, the final state will be different if (A) the transition occurs infinitely slowly, or equivalently if it occurs at any rate with the normal material being insulating rather than metallic, or (B) infinitely fast, or equivalently at any rate with the normal material being a perfect conductor.

Namely, in case (A) the presence of the normal cylinder will not have any effect, and the final state will be the same as depicted in Fig. 7, right panel (the normal metal cylinder is indicated as a dashed rectangle in Fig. 7).

Instead, in case (B), the initial field lines will be $frozen$ in the normal metal cylinder. When the superconductor is cooled it will expel the magnetic field lines to a penetration depth $\lambda_2 < \lambda_1$ but it will have a harder time doing so, because of the boundary condition that magnetic field lines in the normal metal cannot move. As a consequence, the final state in Fig. 8 for the superconductor, denoted by 2', will not be the same as in Fig. 7. In particular, the magnetic field will be more intense near the surface than in the case of Fig. 7. The magnetic field lines will be somewhat different and the associated supercurrent will also be somewhat different.

Is it possible to have two different final states for a simply connected superconductor? Yes, because the boundary conditions are different, the magnetic field outside the superconductor near the upper surface is different for the two situations depicted in Figs. 7 and 8.

More generally, if the normal metal cylinder has a finite electrical conductivity and the cooling process occurs at a finite rate, Joule heat will be dissipated in an amount that depends on the conductivity and the rate. For each different case, with different Joule heat dissipated, the final state of the superconductor will be different. If we imagine this system in the setup of figure 3, where it dumps heat into a reservoir at temperature T_2, the heat dumped will be different in each case and the total entropy generated will be different in each case. There is no contradiction with thermodynamics here, because both the system and the reservoir are reaching a different final state in each case. If we were to compute all the thermodynamics quantities we would find that the laws of thermodynamics hold.

I argue that in a sense what Fig. 8 depicts is the view of superconductors within the conventional theory of superconductivity, where the 'normal metallic cylinder' is immersed inside the superconductor rather than outside as in Fig. 8. Thermodynamic laws will be satisfied if the system is allowed to reach different final states depending on the speed at which the cooling occurs and of the magnitude of its electrical conductivity in the normal state. For example, if the cooling is fast the system will "use up" a large part of its condensation energy in Joule heat rather than in expelling magnetic field, and the final state will have a larger London penetration depth. However, the conventional theory of superconductivity says that there is a unique final state. Hence it is in conflict with thermodynamics.

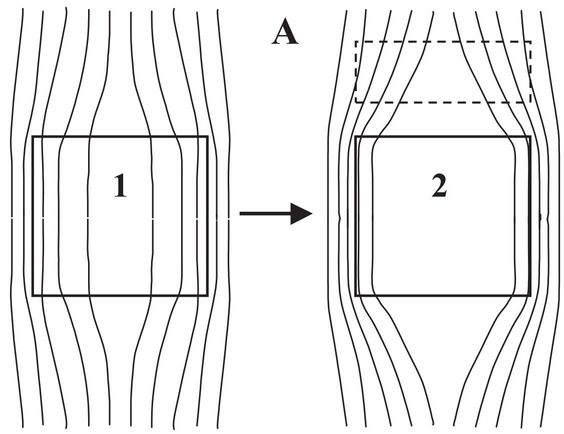

FIG. 7: Schematic depiction of field lines in a cylindrical superconductor of finite height at a higher (left panel) and a lower (right panel) temperature.

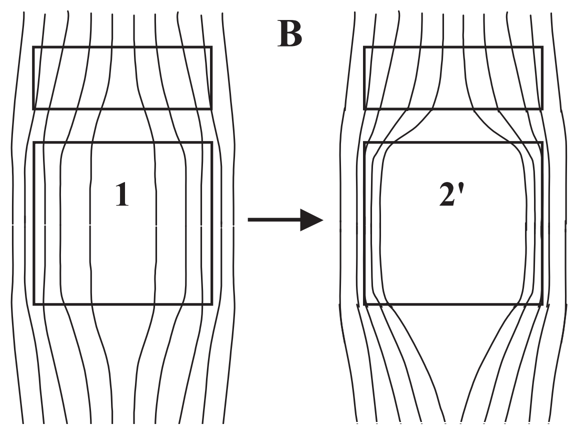

FIG. 8: Same superconducting cylinder as in Fig. 7, with a normal metal cylinder added on top (smaller rectangle) The figure shows schematically the situation where the normal metal is a perfect conductor, or equivalently the transition occurs infinitely fast, so the field lines are frozen in the normal metal.

XV. FURTHER ARGUMENTS

Some readers may think that the situation considered here is not very different from other situations where Joule heat is generated in an amount that depends on the speed of the process, hence that the arguments given here would imply inconsistencies in other situations, hence these arguments cannot be right. That is not so. Let us analyze a couple of simple examples and how they differ from the situation considered here.

A. Magnet and normal conductor

Consider a situation where we approach a permanent magnet by hand to a normal metal. Eddy currents are generated and Joule heat is dissipated, in different amounts depending on the speed of the process and the conductivity of the material. In particular, if we approach the magnet faster the Faraday field is larger and more Joule heat is dissipated. Why is thermodynamics not violated?

The answer is of course that if we approach the magnet faster the eddy currents generate a larger magnetic field that generates a larger force that opposes the motion of the magnet, hence our hand has to do more work to approach the magnet to the metal at a faster speed, and the extra work supplied by us supplies the extra Joule heat generated. Similarly if the conductivity of the material is larger the Joule heat generated is larger, but so are the eddy currents generated and the opposing force.

Instead, for the case of the superconductor considered in this paper there is no external “hand” that can supply variable amounts of work depending on the speed of the process. As discussed, initial and final states of the metal and the reservoir, and hence their energies, are fixed by the initial and final temperatures and are independent of the speed of the process, but the speed of the process is not fixed (it depends on κ) and neither is the amount of generated Joule heat according to the conventional theory.

B. Inductor in a circuit

Let us consider a circuit with an inductor L in series with a resistor R connected to a battery, through which a current circulates. A magnetic field will exist in the inductor, and the magnetic energy stored is

$$U = \frac{1}{2} L I_0^2 \tag{103}$$

with I_0 the initial current circulating. If we now disconnect the battery and short the circuit, the current will decay with time constant $t_0 = L/R$, given by

$$I(t) = I_0 e^{-t/t_0} \tag{104}$$

generating power

$$P(t) = I(t)^2 R. \tag{105}$$

If R is large the Joule heat generated per unit time is large, if R is small it is small, why is energy conservation not violated?

The answer is of course that the *integrated* power, that gives the total Joule heat generated as the current decays to zero, is independent of R and yields of course Eq. (103), as is easily verified. If R is small, the process proceeds very slowly and the power dissipated at any given time is very small, if R is large the process is fast and the power is large, but the time integral and total Joule heat dissipated is always the same, independent of the speed of the process. And of course the origin of the energy dissipated in Joule heat is accounted for, it is the energy that was originally stored in the inductor.

Instead, for the case of the superconductor discussed here, the origin of the energy dissipated in Joule heat is not accounted for, the speed of the process is not determined by the conductivity of the normal electrons, nor does the magnetic field and its time variation depend solely on the normal current since there is also supercurrent. For those reasons the total Joule heat generated is not the same independent of the speed of the process, and is not the same independent of the normal resistivity, and in particular goes to zero if the temperature change proceeds infinitely slowly and/or if the normal state resistivity goes to infinity, and is not zero if it proceeds at a finite rate and the normal state resistivity is finite, leading to the conflict with thermodynamics discussed earlier in the paper.

XVI. RESOLUTION OF THE CONUNDRUM

In this section we propose a qualitative solution to the conundrum discussed in the previous sections.

We don't want to give up on the principle that superconductivity is a thermodynamic state of matter, including the situation where an external magnetic field is present. Nor do we want to give up on the laws of thermodynamics, electromagnetism or mechanics. We propose that there is only one way to resolve this conundrum.

Consider the situation in fig. 8. Imagine that there are electric charges in the normal metal that are completely free to move, and the metal is a perfect conductor. If the mobile charges in the metal move together with the magnetic field lines as the system is cooled, no Joule heat will be generated. This is what happens in a perfectly conducting plasma according to Alfven's theorem [19]: the magnetic field lines are frozen into the fluid, when the fluid moves the magnetic field lines move with it and vice versa, and no Joule heat is generated.

Therefore, if a perfectly conducting fluid residing in the interior of the superconductor moves outward together with the field lines when the system is cooled, no Joule heat will be generated and the system will be able to reach a unique final state independent of the rate at which the field lines move out.

For this to be a possibility this fluid has to be both charge neutral and mass neutral, so that neither charge nor mass accumulation near the surface will occur.

This is possible if there is an outward flow of both electrons and holes. Because holes are not real physical particles, the outward motion of holes is associated with inward rather than outward flow of mass, and it can compensate the outflow of mass due to electrons. The electrons and holes flowing out can drag the magnetic field lines with them, as in a perfectly conducting plasma [19], without energy dissipation.

In previous work, we have explained the dynamics of the Meissner effect within the theory of hole superconductivity as follows [5, 6, 20]: when the phase boundary moves outward, electrons becoming superconducting move outward and acquire azimuthal speed due to the action of the Lorentz force, giving rise to the increasing Meissner current. At the same time, normal holes move outward to compensate for the radial charge imbalance, and the combined action of magnetic and electric fields cause the holes to move radially out without acquiring azimuthal velocity [20]. In this process they transfer azimuthal momentum to the body as a whole without any energy dissipation, thus compensating for the increasing azimuthal momentum of the Meissner current.

We believe the same physics is at play here, as the system is cooled and normal electrons condense into the superfluid, and can explain the contradictions encountered within the conventional theory. In particular, normal holes moving out are subject to a clockwise Lorentz force which can exactly compensate for the counterclockwise force exerted by the Faraday field on them, so that no azimuthal current and no Joule dissipation results.

The details of the process will be discussed elsewhere.

XVII. DISCUSSION

In this paper we have analyzed the process where a type I superconductor in a magnetic field is cooled while always in the superconducting state. We have encountered several problems in trying to understand this process within the conventional theory of superconductivity, and we have suggested that the alternative theory of hole superconductivity [21] may be able to resolve these problems. The same problems would have been encountered if we had considered a process of heating rather than cooling.

The first problem we pointed out is that there has to be a physical mechanism for electrons that go from normal to superconducting in the process of cooling to spontaneously acquire angular momentum, and at the same time for the body to acquire equal and opposite angular momentum. The physical mechanisms by which this happens have not been explained in the literature on conventional superconductivity. We believe the conventional theory cannot explain these processes. In fact, the same question arises in the normal-superconductor phase transition in a magnetic field, or its reverse [22]. We have analyzed these questions within the alternative theory of hole superconductivity and shown how they can be explained with physics that is not part of the conventional theory [5, 20, 22]. The same physics would explain these momentum changes in the context discussed in this paper.

The next problems relate to the action of the Faraday electric field that is necessarily induced when the temperature changes. It will generate a normal current and cause dissipation of Joule heat. We showed that this Joule heat will become arbitrarily large sufficiently close to the phase transition point, and that it will become arbitrarily large if the rate of temperature change is large. .

We have shown that in fact there is normal current originating from two different sources. On the one hand, the Faraday electric field gives rise to a normal current proportional to the density of normal electrons, just like in a normal metal. On the other hand, within the conventional theory the process of condensation leaves behind a momentum imbalance in the normal electron distribution [6, 17], which gives rise to normal current *in the same direction* as that induced by the Faraday field, so it adds to it. The decay of this normal current necessarily gives rise to Joule heating during the process where the London penetration depth changes, either cooling or heating.

Note also that the amount of Joule heat Q_J generated depends both on the speed of the process and on the normal conductivity σ_n, two variables that are not tied to each other, contrary to what happens in the phase transition (see Sect. X and Refs. [16, 18]), and contrary to what happens in a circuit with inductor and resistor (Sect. XV B). So for a given Q_J, we can get the same Q_J by making the process slower by a factor of 2 and increasing σ_n by a factor of 2. Therefore the conflict with thermodynamics that we encounter is not related to the degree by which the system is 'out of equilibrium' during the process.

We have found that the generation of *any* Joule heat in the process considered in this paper is inconsistent with thermodynamics. The only way to make it consistent with thermodynamics within the conventional theory would be to assume that the system reaches different final states depending on the speed of the process, which is itself inconsistent with the conventional theory. By contrast, we showed in this paper that the generation of Joule heat during the normal-superconductor transition is consistent with thermodynamics, assuming Joule heat is dissipated only in the normal region *and* assuming that the process of normal/superfluid conversion is able to transfer momentum to the body without dissipation [6].

In the situation discussed in this paper, the electric field arises in a process where the superfluid density is changing. Therein lies the essential difference with the situations considered in ref. [13] within the conventional theory, where the electric field is due to an electromagnetic wave or an ac current, and is not directly associated with changes in the superfluid density. In that case, it is well established experimentally and theoretically that the action of the electric field on normal electrons gives rise to dissipation. Within the conventional theory of superconductivity the response of normal electrons in those situations and in the situation considered here will be the same. This is necessarily so within the conventional theory in order to satisfy momentum conservation. But it leads to the conundrum discussed in this paper.

Within the conventional theory these normal currents and the resulting Joule heat are unavoidable for a simple reason. There is *no mechanism* that can transfer momentum between electrons and the body as a whole in the conventional theory that does not involve scattering of normal electrons through the same processes that give rise to resistivity in the normal state. Transferring momentum between electrons and the body is necessary to conserve momentum. As we have seen, the total momentum of the body does not change in the process, but the Faraday field imparts the positive ions momentum in the counterclockwise direction that needs to be compensated by 'somebody' giving the body clockwise momentum. In addition, the condensation process involves normal electrons acquiring counterclockwise momentum, which needs to be compensated by the body acquiring more clockwise momentum. Both those processes necessitate transfer of momentum from normal electrons to ions through normal scattering processes in the conventional theory, that give rise to Joule heating as discussed in Sects. VII and VIII and leads to the conflict with thermodynamics.

Instead, within the theory of hole superconductivity there is a mechanism to transfer momentum between electrons and the body that does not involve normal scattering processes and associated Joule heating. It requires that the normal charge carriers are *holes* [5, 6, 20, 22, 23].

We have pointed out that the theory of hole superconductivity [21] has physical elements not contained in the conventional theory that may provide a way to resolve this conundrum. Within this theory the response of the superconductor to ac fields would be similar to the conventional theory [24], consistent with experiment. However, the response to the electric field that arises in the process of electrons condensing or decondensing into or out of the superfluid would not be the same. That is because within this theory those processes are associated with radial outflow of electrons and holes [25], and the magnetic Lorentz force acting on these moving charges will change the effect of the Faraday field on them. In addition, the condensation process does not give rise to normal current within this theory [6]. Qualitatively, within this theory condensation and decondensation is associated with radial flow of a charge-neutral mass-neutral perfectly conducting plasma, which according to Alfven's theorem will flow without dissipation [19].

Appendix A: Calculation of the Joule heat for the normal-superconductor transition

We consider the electromagnetic energy equation

$$\frac{d}{dt}(\frac{H^2}{8\pi}) = -\vec{J}\cdot\vec{E} - \frac{c}{4\pi}\vec{\nabla}\cdot(\vec{E}\times\vec{H}). \tag{A1}$$

for the case where the system makes the transition from normal to superconducting in an applied magnetic field $H_c(1-p)$. The left side represents the change in energy of the electromagnetic field as the magnetic field is expelled from the body, the first term on the right side is the work done by the electromagnetic field on currents in this process, and the second term is the outflow of electromagnetic energy. Integrating over the volume of the body V and over time we find for the change in electromagnetic energy per unit volume

$$\frac{1}{V}\int d^3r \int_0^\infty dt \frac{d}{dt}(\frac{H^2}{8\pi}) = -\frac{H_c^2(1-p)^2}{8\pi}. \tag{A2}$$

since at the end the initial magnetic field $H_c(1-p)$ is completely excluded from the body. From Faraday's law and assuming cylindrical symmetry we have for the electric field generated by the changing magnetic flux at the surface of the cylinder

$$\vec{E}(R,t) = -\frac{1}{2\pi Rc}\frac{d}{dt}\phi(t)\hat{\theta} \tag{A3}$$

where R is the radius of the cylinder and $\phi(t)$ is the magnetic flux throught the cylinder, with $\phi(t=0) = \pi R^2 H_c(1-p)$, $\phi(t=\infty) = 0$. Integration of the second term on the right in Eq. (A1), the energy outflow, over space and time, converting the volume integral to an integral over the surface of the cylinder, using that $H = H_c(1-p)$ at the surface of the cylinder independent of time and Eq. (A3) for the electric field at the surface yields

$$\frac{1}{V}\int_0^\infty dt \oint(-\frac{c}{4\pi})(\vec{E}\times\vec{H})\cdot d\vec{S} = -\frac{H_c^2(1-p)^2}{4\pi}. \tag{A4}$$

This gives the total electromagnetic energy flowing out through the surface of the sample during the transition.

The current $\vec{J}$ in Eq. (A1) flows in the azimuthal direction and is given by the sum of superconducting and normal currents

$$J(r) = J_s(r) + J_n(r) \tag{A5}$$

where $J_s(r)$ flows in the region $r \leq r_0(t)$ and is of appreciable magnitude only within λ_L of the phase boundary, where λ_L is the London penetration depth. $r_0(t)$ is the radius of the phase boundary at time t. Integration of the second term in Eq. (A1) over the superconducting current yields [16]

$$\frac{1}{V}\int d^3r \int_0^\infty dt(-\vec{J}_s \cdot \vec{E}) = \frac{H_c^2}{8\pi}. \tag{A6}$$

This is because the Faraday field decelerates the supercurrent [16] as the phase boundary moves out .

The Joule heat per unit volume generated during the transition is

$$Q_J \equiv \frac{1}{V}\int d^3r \int_0^\infty dt \vec{J}_n \cdot \vec{E} \tag{A7}$$

hence from integrating Eq. (A1) over space and time using Eqs. (A2), (A4), (A5) and (A6) we have

$$-\frac{H_c^2(1-p)^2}{8\pi} = \frac{H_c^2}{8\pi} - Q_J - \frac{H_c^2(1-p)^2}{4\pi} \tag{A8}$$

which implies

$$Q_J = \frac{H_c^2}{4\pi}p \tag{A9}$$

to linear order in p. The entropy generated from Joule heat is then

$$\Delta S_{Joule} = \frac{Q_J}{T} = \frac{H_c^2}{4\pi T}p. \tag{A10}$$

The reason for why in this case there is ‘extra’ condensation energy to generate the Joule heat is that the system is expelling magnetic field $H_c(1-p)$ while being at a temperature where its critical field is larger, i.e. H_c, and correspondingly it has the necessary extra condensation energy.

It is interesting that in this calculation we have not made an assumption of what the speed of the process is, and yet the amount of Joule heat and Joule entropy are completely determined. The reason is, the conditions of the problem completely determine what the speed of the process is. In ref. [6] we showed that if we calculate explicitly the Joule heat from Eq. (A7) over the time the process takes, instead of obtaining Q_J from Eq. (A8) by substraction, the same answer Eq. (A9) is obtained.

Acknowledgments

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