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Thermodynamics of metastable processes in the magnetization of type-I superconductors

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It is shown that in a nonellipsoidal sample of type-I superconductor, for values of the applied magnetic field exceeding a thermodynamic transition field which is defined, the magnetization process is completely governed by a metastable mechanism which is analyzed. The same mechanism is responsible for the frequently observed irreversible behavior.

I. INTRODUCTION

It is well known that the magnetization of type-I superconducting nonellipsoidal samples like cylinders, disks, or slabs, placed in a field parallel to their axes, exhibits an irreversible behavior.[1,2] To date, this behavior does not seem well understood, although many direct experimental observations of the flux structure during magnetization have been reported.[3-8] These observations have revealed a two-stage flux penetration into disks. In the first stage the flux penetrates the samples' corners reversibly, while the second stage, which occurs for a well-defined value of the applied field, is characterized by *migration* of flux tubes towards the center of the sample.

Some general features underlying a unified explanation which we propose for these measurements and observations have been qualitatively described in preliminary reports[9,10] in connection with the existence of a geometry-dependent "magnetic energy barrier." Typical experimental results which strongly support this interpretation, have also been given.

Recently, Clem *et al.*[11] have, independently, discussed the enhancement of the critical current in a type-I superconducting strip, in connection with a Gibbs-free-energy barrier. This analysis was however restricted to a superconducting cylinder with an elliptic cross section of very small dimensions, and the barrier was mainly associated with the field produced by a normal domain which has entered the specimen.

The purpose of this paper is to develop a very simple and quite general thermodynamic proof for the existence of a magnetic energy barrier and a subsequent metastable mechanism, which are strictly dependent on the shape of the specimen. These processes occur as the applied magnetic field (assumed to be uniform) rises above some "ideal" value H_t which will be defined. The analysis leads to a general method for the determination of the magnetic moment as a function of the external field. These results will be illustrated in a forthcoming paper, with many more mathematical details, in the particular case of an infinite slab of rectangular cross section.

For the sake of definiteness the typical example of a slab will serve to support most of the arguments which follow, although the conclusions we will arrive at are not restricted to particular specimen shapes.

II. THERMODYNAMIC TRANSITION FIELD

Consider a sample the half cross section of which is represented in Fig. 1, submitted to a uniform magnetic field parallel to the Oz axis. As the field is increased from zero, an intermediate state begins to appear in the vicinity of the edges, to prevent the resultant field in these regions from rising to infinity. This corresponds to a reversible stage of magnetization.

The particular properties of the field distribution in regions which are in the intermediate state, have been investigated by several authors.[12,13] The major result is that in the absence of applied

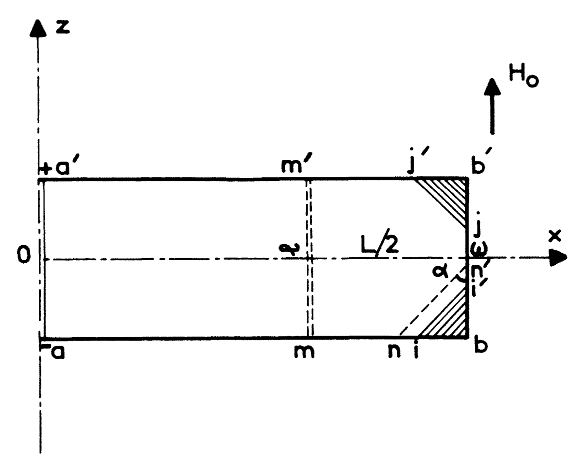

FIG. 1. Schematic of the half cross section of a type-I superconducting slab, showing the intermediate-state structure in the edges, a central normal domain aa', and a possible intermediate position mm' during the process of migration.

currents, the magnetostatic field in these regions must be uniform with a magnitude equal to the value H_c of the critical field in the material. This is valid on a macroscopic scale, i.e., in a volume containing a sufficiently large number of normal and superconducting domains. In addition, on the same scale, complications arising from the distortion of the lines of force, branching and corrugation, in the neighborhood of the surface of the sample (within a distance on the order of the domain spacing) can be ignored. Throughout this paper the dimensions of the sample and the volumes of the regions of the specimen in the intermediate state, will be assumed to be large enough to allow such surface effects to be discarded, along with the surface energy of the normal-superconducting walls.

As the field is increased further, penetration of the flux into the bulk of the sample could be expected, at first sight, to occur at the lowest value for which the presence of a domain in the middle of the slab begins to be favorable from a thermodynamic point of view.

With a view to defining this threshold value of the applied field, we will first establish the expression of the increment ΔG of the thermodynamic potential G, between the states (I) and (II), in which the magnetic field distribution is at equilibrium, for the same value of the applied field $\vec{H}_0$, and defined as follows: (I) the sample is in the diamagnetic state, except perhaps for penetration in the edges; (II) the same state as before with an extra normal domain which is assumed to have freely penetrated the diamagnetic region (Fig. 2).

Assume for clarity that the magnetization of the sample is obtained with currents in a coil. Whatever may be the assumed domain configuration, the magnetic contribution to the suited thermodynamic potential G is given by

$$G_M = \int \int [\vec{H}\cdot\delta\vec{B} - \delta(\vec{B}\cdot\vec{H})]\, d^3r$$

$$= - \int \int \vec{B}\cdot\delta\vec{H}\, d^3r. \tag{1}$$

The integration over the volume is extended to the whole space and the integration over $\vec{H}$ is extended to the magnetization process, when the applied field is varied from 0 to H_0.

In (1), $\vec{H}$ represents the applied field $\vec{H}_0$ or the resultant magnetostatic field as well. This latter field is the sum of $\vec{H}_0$ and the demagnetizing field deriving from the polarization potential ϕ_p due to the magnetic masses

$$\vec{H} = \vec{H}_0 - \text{grad}\phi_p . \tag{2}$$

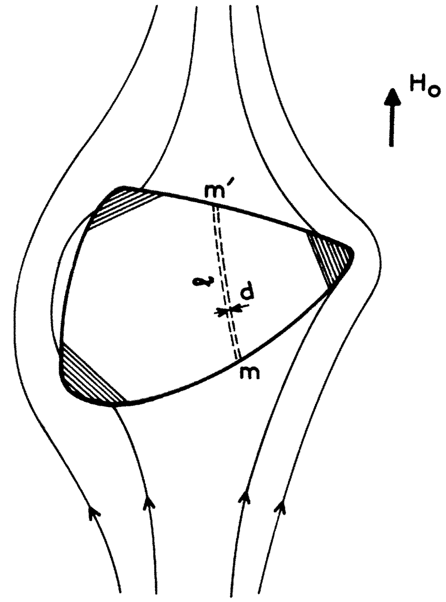

FIG. 2. In a sample of arbitrary shape the intermediate-state structure occurs in the edges as the local field is larger than H_c . mm' is a normal domain position, the stability of which is discussed in the text.

We shall keep $\vec{H}$ for convenience in the following.

In order to calculate the value of G_M in the states (I) and (II) we can imagine a system consisting of superconducting matter and vacuum (in place of the matter in normal state), in the same configuration (Fig. 2), viz., with structure in the edges and, in the state (II), the extra domain mm' (dimensions l, d, volume $V_d \sim ld^2$), lying along a line of force of the magnetostatic field. If such a device is magnetized up to the value $\vec{H}_0$ of the applied field, the final magnetic state is strictly the same as the real one. It follows, from first law, that G_M can be, as well, calculated in this way.

Since $\vec{B} = 0$ in the diamagnetic matter, the integration over the volume is in fact restricted to the normal domains of the regions in the intermediate state, and to the outside space of the sample which includes the generating currents. Thus we can take $\vec{B} = \mu_0\vec{H}$ and write in place of (1)

$$G_M = -\tfrac{1}{2}\mu_0 \int_{\substack{\text{normal and}\\ \text{outside space}}} H^2\, d^3r. \tag{3}$$

The extra domain which is freely penetrated by the flux, is in magnetic equilibrium. Except in the vicinity of its free ends, the external field distribution is only slightly modified. At every point, the "unperturbed" field H_I, in the state (I), is now increased by an amount $\Delta\vec{H}$. This increment can be regarded as deriving from the variation $\Delta\phi_p$ of the polarization potential, resulting from the deficit of magnetic masses which were located in place of the domain

$$\Delta\vec{H} = -\,\mathrm{grad}\Delta\phi_p . \tag{4}$$

The magnitude of the field inside the domain $H_{II}(d)$, or for the sake of compactness H_d, can be shown, in a self-consistent way, to approach the mean value $H_I(d) = (\phi_m - \phi_{m'})/l$ of the field along the line of force, in state (I); here ϕ_m and $\phi_{m'}$ include both the polarization potential and the potential of the applied field which is defined outside the generating currents. If that is assumed, from $\vec{H}_I(d)+\vec{I}_I(d)=0$ and $I_{II}(d)=0$, the increase of polarization intensity in the domain is then $\Delta I_d = I_{II}(d) - I_I(d) \sim H_I(d)$. It follows that the main contribution to the increase of ϕ_m is the potential created by the excess surface density $-H_I(d)$ at the very free end m. This increase is readily shown to be on the order of $\Delta\phi_m \sim -H_I(d)d$. Similarly, $\Delta\phi_{m'} \sim H_I(d)d$. Thus, H_d can be written

$$H_d = (\phi_m + \Delta\phi_m - \phi_{m'} - \Delta\phi_{m'})/l$$
$$= [(\phi_m - \phi_{m'})/l][1 + O(d/l)]. \tag{5}$$

From the above discussion the variation of the G_M function between states (I) and (II) can now be written

$$\Delta G_M = G_M(\mathrm{II}) - G_M(\mathrm{I})$$
$$= -\tfrac{1}{2}\mu_0\left(\int_{\substack{\text{normal and outside}\\ +\text{ extradomain}}} H_{II}^2\, d^3r - \int_{\substack{\text{normal and}\\ \text{outside}}} H_I^2\, d^3r\right)$$
$$= -\tfrac{1}{2}\mu_0 H_d^2 V_d - \tfrac{1}{2}\mu_0 \int_{\substack{\text{normal and}\\ \text{outside}}} (H_{II}^2 - H_I^2)\, d^3r. \tag{6}$$

The main contribution of the extradomain has been separated out. Since $\Delta\vec{H}$ derives from a magnetic potential $\Delta\phi_p$ [Eq. (4)] the volume integral can be transformed as follows:

$$\int (H_{II}^2 - H_I^2)\, d^3r = \int (\vec{H}_I + \vec{H}_{II})\cdot\Delta\,\vec{H}\, d^3r$$
$$= -\int (\vec{H}_I + \vec{H}_{II})\cdot \mathrm{grad}\Delta\phi_p\, d^3r$$
$$= -\int \mathrm{div}[(\vec{H}_I + \vec{H}_{II})\Delta\phi_p]\, d^3r$$
$$-\int \mathrm{div}(\vec{H}_I + \vec{H}_{II})\Delta\phi_p\, d^3r.$$

The second term in the right-hand member is zero since $\mathrm{div}\,\vec{H} = 0$ everywhere in normal and outside space. Furthermore, the normal component of $\vec{H}$ is continuous at the surface of generating currents. Thus, the first term can be transformed into an integral extended to the surface of the sample only. Since $\vec{H}_I$ is purely tangential, and the same for $\vec{H}_{II}$, except at the free ends of the extra domain, we obtain

$$\int_{\substack{\text{normal and}\\ \text{outside}}} (H_{II}^2 - H_I^2)\, d^3r = \int_{\substack{\text{free domain}\\ \text{surfaces}}} \vec{H}_{II}\cdot\vec{n}\Delta\phi_p\, d^2r . \tag{7}$$

But at the free surfaces of the domain, $\Delta\phi_p$ is equated to $\Delta\phi_m$ or $\Delta\phi_{m'}$ [the potential of $\vec{H}_0$ does not vary between (I) and (II)] of order $\pm H_d d$, as shown above. Thus the right-hand member of Eq. (7) is on the order of $H_d^2 d^3 = (d/l)H_d^2 V_d$, and consequently ΔG_M can be written

$$\Delta G_M \simeq -\tfrac{1}{2}\mu_0 H_d^2 V_d[1 + O(d/l)]. \tag{8}$$

On the other hand, the variation of the condensation energy between states (I) and (II) is $\tfrac{1}{2}\mu_0 H_c^2 V_d^2$. It follows that the resultant increase of the thermodynamic potential G is given by

$$\Delta G = \tfrac{1}{2}\mu_0 V_d (H_c^2 - H_d^2) \tag{9}$$

up to order d/l. It can be concluded that a state such as (II) is more stable than (I), as H_0 reaches the value defined by

$$H_d = H_c . \tag{10}$$

For an infinite elliptic cylinder placed in a field normal to its broadest plane of symmetry

$$\phi_m - \phi_{m'} = mm'[\,l/(l+L)]H_0. \tag{11}$$

l, L are the lengths of the small and large axes of the ellipse. The field is uniform inside the sample and the condition (10) leads to the transition of the sample as a whole into the intermediate state.

Instead, in the case of a slab of rectangular cross section (Fig. 1), assumed in a completely diamagnetic state, detailed calculations[14] show that the potential difference 2ϕ at abscissa x is determined by the equation

$$x = (\phi_a/H_0)[E(\theta, (\phi_a^2 - \phi_b^2)^{1/2}/\phi_a)$$
$$- (\phi_b^2/\phi_a^2)F(\theta, (\phi_a^2 - \phi_b^2)^{1/2}/\phi_a)], \tag{12}$$

where F, E are elliptic integrals of the first and second kind, and $\theta = \sin^{-1}[(\phi_a^2 - \phi^2)/(\phi_a^2 - \phi_b^2)]$. ϕ, and thereby the field $H_d(x)$, monotically decreases from a to b. The greatest value occurs between a and a' on the axis. It follows that the lowest threshold value of the applied field corresponds to the appearance of a straight line domain along the axis. This value is determined, from Eqs. (5) and (10) by

$$(\phi_a - \phi_{a'})/l = H_c . \qquad (13)$$

By using Eq. (12) applied to $x=0$, $\phi=\phi_a$, and $x=x_\omega=\frac{1}{2}L$, $\phi=\phi_b$, this yields, for $l \ll L$

$$H_0 \simeq (l/L)\{1-(l/\pi L)(1+\ln[4\pi L/l])\}H_c .$$

Note, by comparing with Eq. (11), that this result is close to $(1-\nu)H_c$, in which ν is the demagnetizing factor of the elliptic cylinder inscribed in the slab ($\nu \simeq l/L$).

In more general cases, for a sample of arbitrary shape [Fig. 3(a)], consider, as the applied field is increased from zero, the *first* pair of points a, a' belonging to the same line of force, located on the surface of the sample, and such that

$$\phi_a - \phi_{a'} = aa'H_c .$$

Then a one-domain phase, characterized by a normal domain lying along aa' is thermodynamically possible. The threshold value H_t of the applied field for which this just occurs will be called the *thermodynamic transition field*. For not overly complicated shapes, it can be recognized that a and a' coincide with the points at which an external flux line meets the matter in the diamagnetic state (Fig. 3). Furthermore, it must be noted that the convenient assumption of the domain lying along a line of force is not essential. The lowest threshold is likely to correspond to a straight line between two definite points a, a' with some subsequent rearrangement of the field distribution.

As H_0 is increased beyond H_t, the one-domain phase spreads out into a partial intermediate state around aa' [Fig. 3(b)]. In addition, due to the requirement of internal stability discussed above, as the number of domains is large enough, they all become parallel to a common straight-line direction.

For further increase of the field, this partial intermediate state progressively extends over the whole volume of the sample which finally transits into the normal state.

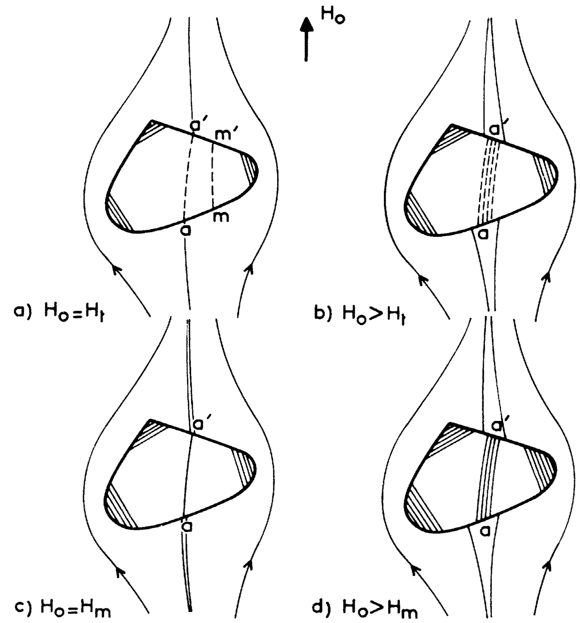

FIG. 3. Internal configuration of the magnetization in a sample of arbitrary shape. (a) One-domain, (b) multidomain thermodynamic phase; (c) one-domain, (d) multidomain metastable phase.

III. METASTABLE MECHANISM

The question now arises as how this thermodynamic configuration of absolute stability can be attained. Now, in superconductors the well-known fluxoid theorem,[12] well confirmed by direct observations,[3-8] prevents a flux tube from being spontaneously created in the bulk of a specimen, and thereby imposes a migration from an edge structure as schematically shown in Fig. 4. As a result it can be ascertained that (i) *a domain can only reach a given position inside the sample by migration from a peripheral region in which the field has the critical value*; in addition, for the migration to be possible, (ii) *a continuous set of intermediate positions must exist between the edge and the given place, along which the condition* (10) *is obeyed.*

Consider now a position such as mm' in Figs. 1 or 3(a). When $H_0=H_t$, since aa' is the first couple for which $\phi_a-\phi_{a'}=aa'H_c$, we have

$$\phi_m - \phi_{m'} < mm'H_c ,$$

so that for any intermediate position of a domain between aa' and a limiting position such as ii' in the edge structure

$$H_d < H_c ,$$

whence, from Eq. (9),

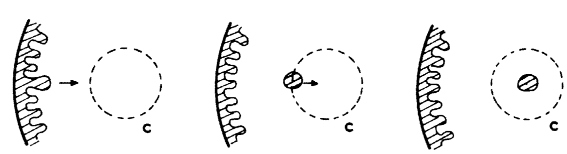

FIG. 4. By migration from the edge structure of the sample a flux tube can reach a position inside any given contour C, since the requirement of the fluxoid theorem drops as the contour is penetrated by the tube.

$\Delta G > 0$.

This proves that the migration is impeded by a kind of magnetic energy barrier and that a further increase of the applied field is needed for the migration to take place. Thus the sample remains in an almost complete diamagnetic state, although a configuration with a bundle of domains somewhere in the bulk would be of lower potential. The new threshold value H_m of H_0 must be such that $\Delta G \leq 0$ all along some definite path for the domain. H_m may be appreciably larger than H_t. In fact for $H_0 > H_m$, $\phi_m - \phi_{m'} > lH_c$, whence, according to Eq. (9), $\Delta G < 0$. Migration takes place up the vicinity of aa' but, of course, due to the very presence of the migrating flux tubes, the field distribution undergoes some local change so that the field inside the tubes recovers the critical value.

For the reasons just discussed, the configuration which appears beyond the thermodynamic threshold H_t can be regarded as metastable. Beyond H_m, this configuration consists of an increasing number of migrated domains in the bulk of the sample, and is similar to the thermodynamic configuration, except for a certain delay in the values of the applied field [Figs. 3(c) and 3(d)].

It is worth stressing that the threshold field magnitudes H_t, H_m are strongly dependent on the geometry of the sample. In the slab of Fig. 1 no domain can exist in position nn'. Indeed, we have

$$\phi_n - \phi_{n'} = niH_{ni} + ii'H_c + n'i'H_{n'i'}\,. \tag{14}$$

H_{ni}, $H_{n'i'}$ stand for the mean value of the tangential field along ni, $n'i'$. Ignoring the fine structure of the magnetization in the edge, the tangential component of the field decreases from $H_c \sin\alpha$ by going from n to i. It follows that

$$\phi_n - \phi_{n'} < (ni\sin\alpha + ii' + n'i'\cos\alpha)H_c = nn'H_c\,,$$

which leads to $H_d < H_c$ along nn'. In a more intuitive way, if the latter inequality were not satisfied, the intermediate-state structure should, at least, extend up to nn'.

Instead, as the two symmetrical structures meet each other at ω, in the equatorial plane, the migration can start since, in that configuration, for any mm'

$$\phi_m - \phi_{m'} > \phi_i - \phi_{j'} = 2ii'H_c > mm'H_c\,.$$

Similar arguments can be given for edge structures which may occur in arbitrary shapes.

Particular forms could perhaps be imagined, in which (10) would be obeyed along a definite continuous set of positions between aa' and the edge structure. A much more special case is presented by volumes in which the field is completely uniform, such as an ellipsoid. Then, a demagnetizing factor ν can be defined, and (10) is obeyed at once for all lines parallel to $\vec{H}_0$, whereas the threshold fields take on the common value

$$H_m = H_t = (1-\nu)H_c\,.$$

IV. MAGNETIZATION LAW AND IRREVERSIBLE BEHAVIOR

As H_0 has just overcome the migration threshold H_m, the ideal configuration of minimum potential would consist of a bundle of domains of definite extension in the bulk diamagnetic region of the sample. If this were true, the magnetic moment would exhibit a discontinuous drop around H_m. The reason why this is not observed in the actual experimental situation[14,15] can be easily understood in the light of the above discussion.

Assume that a few domains have just migrated into position aa' (Fig. 1). It is readily realized that, on account of the resulting increase of magnetic masses in a, a', the field around ω is reduced. It follows that the two symmetrical edge structures, which have just met in the equatorial plane, now separate. Thus, after migration every flux tube again *raises* the energy barrier behind itself, so that a further increase of the field is required for the migration to proceed further. The same rule obtains whatever the edge structure from which the migration initially moves. As a result, *the over-all decreasing part of the magnetization law* $-M(H_0)$ *is governed by the migration condition* (10). Thus, in this range of applied field, the magnetization is also of metastable character (Fig. 5).

The metastable mechanism just discussed offers at once, a simple interpretation of the usually observed irreversible behavior of magnetization.

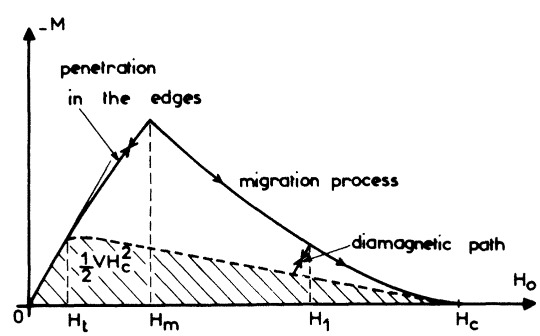

FIG. 5. General behavior of the magnetic moment of a type-I superconducting slab as a function of the applied field. The hatched area relates to the ideal thermodynamic process. A diamagnetic path is shown below $H_1 > H_m$.

In fact the magnetization is reversible up to the beginning of the migration process, i.e., for $H_0 \leq H_m$. In this stage, the small penetration in the edges explains the observed[14] slight curvature of the function $-M(H_0)$ (Fig. 5).

The reversible process would correspond to the ideal thermodynamic phase and would give rise to a magnetization curve of area $\frac{1}{2} V H_c^2$ (V is the volume of the sample), as shown in Fig. 5.

Another interesting feature associated with the irreversible behavior is the existence of the "diamagnetic paths," first mentioned by Schweitzer and co-workers[16] in type-II materials and easily observed in type I as well.[2] If the field is decreased below some value $H_1 > H_m$ (Fig. 5) the total flux which has entered the sample by migration is confined inside by the energy barrier, so that the magnetic moment approximately responds, at least in a first stage, to the equation

$$M + H_0 = Ct .$$

This is the equation of a parallel to the diamagnetic line. The latter remark suggests that the present analysis and conclusions could be applied, to a certain extent, to type-II superconductors.

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