# <span id="page-0-0"></span>**Critical fields of superconductors with magnetic impurities**

V. G. Koga[n](https://orcid.org/0000-0001-8329-2691) **a** and R. Prozoro[v](https://orcid.org/0000-0002-8088-6096)  $\bullet^*$ 

*Ames National Laboratory, U.S. Department of Energy (DOE)*

*and Department of Physics & Astronomy, Iowa State University, Ames, Iowa 50011, USA*

(Received 23 June 2022; accepted 27 July 2022; published 4 August 2022)

The upper critical field  $H_{c2}$ , the field  $H_{c3}$  for nucleation of the surface superconductivity, and the thermodynamic field *Hc* are evaluated within the weak-coupling theory for the isotropic *s*-wave case with arbitrary transport, and pair-breaking scattering. We find that, for the standard geometry of a half-space sample in a magnetic field parallel to the surface, the ratio  $R = H_{c3}/H_{c2}$  is within the window  $1.55 \lesssim R \lesssim 2.34$ , regardless of temperature or the scattering type. While the nonmagnetic impurities tend to flatten the  $R(T)$  variation, magnetic scattering merely shifts the maximum of  $\mathcal{R}(T)$  to lower temperatures. Surprisingly, while reducing the transition temperature, magnetic scattering has a milder impact on  $R$  than nonmagnetic scattering. The surface superconductivity is quite robust; in fact, the ratio  $\mathcal{R} \approx 1.7$  even in the gapless state. We used Eilenberger's energy functional to evaluate the condensation energy  $F_c$  and the thermodynamic critical field  $H_c$  for any temperature and scattering parameters. By comparing  $H<sub>c2</sub>$  and  $H<sub>c</sub>$ , we find that, unlike transport scattering, the pair-breaking pushes materials toward type-I behavior. We find a peculiar behavior of *Fc* as a function of the pair-breaking scattering parameter at the low-*T* transition from gapped to gapless phases, which has recently been associated with the topological transition in the superconducting density of states.

DOI: [10.1103/PhysRevB.106.054505](https://doi.org/10.1103/PhysRevB.106.054505)

### **I. INTRODUCTION**

The question of the critical fields  $H_{c2}$  and  $H_{c3}$  is practically relevant since it is directly related to the critical temperature  $T_c(H)$  where superconductivity emerges in the applied magnetic field *H*. In type-II materials at a fixed *T* , in the increasing field, the vortex phase in the bulk is destroyed at  $H_{c2}$ , but the superconductivity may survive in a coherence-length-deep surface layer up to  $H_{c3}$ .

In recent decades, the interest in limiting fields was further fueled by the significant progress in superconducting resonator cavities used in particle accelerators [\[1,2\]](#page-5-0) and even more recently in the hardware for superconducting circuitsbased quantum computing  $[3,4]$ . Of particular interest are effects of disorder that influence cavities quality factors and superconducting qubit coherence times [\[1,5\]](#page-5-0).

The ratio  $\mathcal{R} = H_{c3}/H_{c2}$  for the applied field parallel to the surface of the isotropic superconducting half-space has been evaluated by Saint-James and DeGennes (SJDG) [\[6\]](#page-5-0) by solving the linearized Ginzburg-Landau (GL) equations for the order parameter  $\Delta$  subject to the boundary condition of a vanishing normal gradient  $\nabla_n \Delta = 0$  at the sample surface. Their seminal result is  $\mathcal{R} = 1.695$ . Since then, surface superconductivity has been observed in many experiments, but the ratio  $R$  varied depending on surface quality, sample anisotropy, setup geometry, scattering, and temperature  $[7-11]$ . Theoretically, effects of material anisotropy have been discussed in Ref.  $[12]$ , where it was shown that, for sufficiently high anisotropy for some surface orientation, the ratio  $\mathcal R$  may fall under unity. In other words, surface superconductivity does not exist.

An interesting development came recently, showing that, within microscopic Bardeen-Cooper-Schrieffer (BCS) theory,  $\mathcal{R}(T)$  has a maximum at intermediate temperatures which, however, disappears with increasing transport scattering [\[13\]](#page-5-0). In this contribution, we extend this study to the case when both magnetic and nonmagnetic scattering channels are present. The discussion is limited to isotropic material with an isotropic Fermi surface and *s*-wave order parameter. Given that  $H_{c2}$  is enhanced by nonmagnetic transport scattering whereas it is suppressed by magnetic impurities [\[14\]](#page-5-0), the question of the effect of magnetic impurities on  $H<sub>c3</sub>$  is not obvious.

### **II. THE PROBLEM OF**  $H_{c2}$  **AND**  $H_{c3}$

Consider an isotropic material with both magnetic and nonmagnetic scatterers;  $\tau_m$  and  $\tau$  are the corresponding average scattering times. The problem of the second-order phase transition at  $H_{c2}$  and  $H_{c3}$  is addressed on the basis of Eilenberger's quasiclassical version of Gor'kov's equations for normal and anomalous Green's functions *g* and *f* . At the second-order phase transition,  $g = 1$ , and we are left with a linear equation for *f* [\[15,16\]](#page-5-0):

$$
(2\omega^{+} + \mathbf{v} \cdot \mathbf{\Pi}) f = \frac{2\Delta}{\hbar} + \frac{\langle f \rangle}{\tau^{-}},
$$
  
\n
$$
\omega^{+} = \omega + \frac{1}{2\tau^{+}},
$$
  
\n
$$
\frac{1}{\tau^{\pm}} = \frac{1}{\tau} \pm \frac{1}{\tau_{m}}.
$$
  
\n(2)

<sup>\*</sup>prozorov@iastate.edu

<span id="page-1-0"></span>Here, **v** is the Fermi velocity,  $\Pi = \nabla + 2\pi i \mathbf{A}/\phi_0$  with the vector potential **A** and the flux quantum  $\phi_0$ . Also,  $\Delta(r)$  is the order parameter; Matsubara frequencies are defined by  $\omega = \pi T(2n + 1)$  with an integer *n*; in the following (except some final results), we set  $\hbar = k_B = 1$ ;  $\langle ... \rangle$  stand for averages over the Fermi surface. Solutions  $f$  of Eq. [\(1\)](#page-0-0) along with  $\Delta$ should satisfy the self-consistency equation:

$$
\frac{\Delta}{2\pi T} \ln \frac{T_{c0}}{T} = \sum_{\omega > 0} \left( \frac{\Delta}{\omega} - \langle f \rangle \right),\tag{3}
$$

where  $T_{c0}$  is the critical temperature in the absence of pairbreaking scattering.

Helfand and Werthamer [\[17\]](#page-5-0) had shown that, at the secondorder phase transition at  $H_{c2}$ , the order parameter satisfies a linear equation

$$
\Pi^2 \Delta = k^2 \Delta. \tag{4}
$$

It was realized later that this equation holds at any secondorder transition from normal to superconducting state away from  $H_{c2}$ , e.g., in proximity systems or at  $H_{c3}$ , provided  $k^2 = -1/\xi^2$  satisfies the self-consistency equation of the theory [\[18,19\]](#page-5-0). It turned out that the coherence length so evaluated depends not only on temperature and scattering but also on the magnetic field (except in the dirty limit or near *Tc*). In this sense, Eq. (4) in fact differs from the linearized GL equation that forms the basis for SJDG prediction of the surface superconductivity at  $H_{c3}$  [\[6\]](#page-5-0). It is worth noting that, if  $\xi$  would have been *H* independent, the ratio  $H_{c3}/H_{c2}$  would have been a constant equal to 1.695 at all temperatures. As was shown in Ref. [\[13\]](#page-5-0), this is not so (except for the dirty limit).

Thus, the order parameters at both  $H_{c2}(T)$  and  $H_{c3}(T)$ satisfy the same Eq. (4). The difference, however, comes from boundary conditions:  $\Delta(\mathbf{r})$  should be finite everywhere for  $H_{c2}$ , whereas  $\nabla_n \Delta(\mathbf{r}) = 0$  at the sample surface for  $H_{c3}$  ( $\nabla_n$ is the gradient of  $\Delta$  along the normal to the sample surface).

At any second-order phase transition,  $\Delta \rightarrow 0$ , and one can deal with linear Eq. [\(1\)](#page-0-0). Repeating the derivation of Ref. [\[18\]](#page-5-0), one finds (see the outline in Appendix [A\)](#page-4-0)

$$
\langle f \rangle = \Delta \frac{2\tau^{-}S}{2\omega^{+}\tau^{-} - S},\tag{5}
$$

where *S* is given by a series:

$$
S = \sum_{j,m=0}^{\infty} \frac{(-q^2)^j}{j!(2m+2j+1)} \left[ \frac{(m+j)!}{m!} \right]^2 \left( \frac{\ell^+}{\beta^+} \right)^{2m+2j}
$$
  
 
$$
\times \prod_{i=1}^m \left[ k^2 + (2i-1)q^2 \right], \qquad q^2 = \frac{2\pi H}{\phi_0}, \qquad (6)
$$

where

$$
\ell^+ = v\tau^+, \qquad \beta^+ = 1 + 2\omega\tau^+.
$$
 (7)

This sum can be transformed to an integral, which is more amenable for the numerical work [\[19\]](#page-5-0):

$$
S = \sqrt{\frac{\pi}{u}} \int_0^1 \frac{d\eta (1 + \eta^2)^\sigma}{(1 - \eta^2)^{\sigma + 1}} \left[ \operatorname{erfc} \frac{\eta}{\sqrt{u}} - \cos(\pi\sigma) \operatorname{erfc} \frac{1}{\eta \sqrt{u}} \right].
$$
\n(8)

Here,

$$
u = \left(\frac{q\ell^+}{\beta^+}\right)^2 = \frac{h}{[P^+ + t(2n+1)]^2},\tag{9}
$$

where the reduced field *h*, temperature *t*, and the scattering parameters  $P^{\pm}$  are introduced:

$$
h = H \frac{\hbar^2 v^2}{2\pi \phi_0 T_{c0}^2}, \quad t = \frac{T}{T_{c0}}, \quad P^{\pm} = \frac{\hbar}{2\pi T_{c0} \tau^{\pm}} \quad (10)
$$

( $\hbar$  is written explicitly to stress that *h* and  $P^{\pm}$  are dimensionless). Note that  $P^{\pm} = P \pm P_m$ , where

$$
P = \frac{\hbar v}{2\pi T_{c0}\tau}, \qquad P_m = \frac{\hbar v}{2\pi T_{c0}\tau_m}.
$$
 (11)

The parameter  $\sigma$  is defined as

$$
\sigma = \frac{1}{2} \left( \frac{k^2}{q^2} - 1 \right) = -\frac{1}{2} \left( \frac{1}{q^2 \xi^2} + 1 \right).
$$
 (12)

At  $H_{c2}$ ,  $\sigma = -1$  and

$$
S(u) = \sqrt{\frac{\pi}{u}} \int_0^1 \frac{d\eta}{1 + \eta^2} \left[ \text{erfc} \frac{\eta}{\sqrt{u}} + \text{erfc} \frac{1}{\eta \sqrt{u}} \right]. \tag{13}
$$

Near  $T_c$ , the order parameter satisfies the linearized GL equation  $-\xi^2 \Pi^2 \Delta = \Delta$ , and at *H<sub>c3</sub>*, SJDG obtained  $\xi^2 q^2 =$ 1.695 [\[6\]](#page-5-0).

Therefore, at  $H_{c3}$ , we get

$$
\sigma = -\frac{1}{2} \left( \frac{1}{1.695} + 1 \right) \approx -0.795. \tag{14}
$$

Thus, to calculate  $H_{c3}(t, P, P_m)$  with the help of Eqs. (3) and (5), one has to use *S* of Eq. (8) with  $\sigma = -0.795$ .

For numerical work, we recast the self-consistency equation to the dimensionless form:

$$
-\ln t = \sum_{n=0}^{\infty} \left[ \frac{1}{n + \frac{1}{2}} - \frac{2tS}{2t(n + \frac{1}{2}) + P^+ - SP^-} \right].
$$
 (15)

The calculated ratio  $\mathcal{R} = H_{c3}/H_{c2}$  as function of the reduced temperature  $T/T_{c0}$  for a few values of scattering parameters  $P$  and  $P_m$  is shown in the upper panel of Fig. [1;](#page-2-0) the lower panel shows the same results plotted vs  $T/T_c$ . One can see that the maximum of  $R$  shifts to lower  $T$  with increasing transport scattering *P*. Effects of magnetic scattering are mostly in suppressing the actual critical temperature  $T_c$ and larger values of  $R$  at low temperatures as compared with purely transport scattering.

It was shown in Ref. [\[13\]](#page-5-0) that, in the absence of magnetic impurities and a strong transport scattering, the ratio  $\mathcal{R}(T)$ flattens, and the *T* dependence disappears in the dirty limit in which  $\mathcal{R}(T) \approx 1.7$  at all *T*. This is due to the disappearing field dependence of the coherence length  $\xi$  [\[19\]](#page-5-0) in this limit. It is thus instructive to see that the magnetic scattering does not change this qualitatively, see the upper panel of Fig. [2.](#page-2-0)

Hence, magnetic impurities do not drastically change the behavior of  $H_{c3}$  relative to  $H_{c2}$ . We find that, within the isotropic *s*-wave theory, for the standard geometry of a halfspace sample in a field parallel to the surface, the ratio  $\mathcal{R} =$  $H_{c3}/H_{c2}$  is within the window  $1.55 \lesssim R \lesssim 2.34$ , regardless of temperature and magnetic or nonmagnetic scattering.

<span id="page-2-0"></span>

FIG. 1. (a)  $\mathcal{R}(P, P_m) = H_{c3}/H_{c2}$  vs  $T/T_{c0}$  for the scattering parameters indicated. (b) The same plotted vs the actual reduced temperature  $T/T_c(P_m)$ .

On the dirty side (with strong transport scattering), the maximum of  $\mathcal{R}(T)$  moves to  $T \approx 0$ , as is seen in the lower panel of Fig. 2. Effects of pair breaking here are not drastic; even for the gapless situation  $(0.128 < P_m < 0.14, [16])$  $(0.128 < P_m < 0.14, [16])$  $(0.128 < P_m < 0.14, [16])$ , we still have  $\mathcal{R} \approx 1.7$ .

# **III. TYPE OF SUPERCONDUCTIVITY AND MAGNETIC IMPURITIES**

The basic Eqs.  $(1)$  and  $(3)$  can be obtained minimizing the energy functional as is done in Eilenberger's paper [\[15\]](#page-5-0) for exclusively transport scattering:

$$
\Omega = N(0) \left[ \Delta^2 \ln \frac{T}{T_{c0}} + 2\pi T \sum_{\omega > 0} \left( \frac{\Delta^2}{\omega} - \langle I \rangle \right) \right], \qquad (16)
$$

$$
I = 2\Delta f + 2\omega(g - 1) + \frac{f\langle f \rangle}{2\tau} + \frac{g\langle g \rangle - 1}{2\tau^+}.
$$
 (17)



FIG. 2. (a)  $\mathcal{R}(T) = H_{c3}/H_{c2}$  vs  $T/T_{c0}$  for strong transport scattering and a set of  $P_m$  values for magnetic scattering. (b)  $\mathcal R$  vs pair-breaking scattering parameter *Pm* at a low reduced temperature  $T/T_c(P_m) = 0.1$  for a set of *P* values of transport scattering. Note: The maximum  $P_m$  possible is 0.1404.

The function *g* in Eq. (17) is an abbreviation for  $\sqrt{1 - f^2}$ . The free energy difference between superconducting and normal states is obtained by substituting solutions of Eq. [\(1\)](#page-0-0) in  $\Omega$ . Considering the self-consistency equation, we obtain for the condensation energy density  $F_c = F_n - F_s$ :

$$
\frac{F_c}{2\pi TN(0)} = \sum_{\omega > 0} \left\{ \Delta f + 2\omega(g - 1) + \frac{f\langle f \rangle}{2\tau} + \frac{g\langle g \rangle - 1}{2\tau^+} \right\}.
$$
\n(18)

This expression reduces to known BCS results for isotropic *s*-wave cases with or without magnetic impurities [\[20\]](#page-5-0). For the uniform zero-field state, the averaging brackets can be omitted, and the scattering part is  $-f^2/\tau_m$ . Introducing the

<span id="page-3-0"></span>dimensionless order parameter  $\delta = \Delta/2\pi T_{c0}$  one has

$$
\frac{F_c}{4\pi^2 T_{c0}^2 N(0)} = t \sum_{n=0}^{\infty} \left[ \delta f + t(2n+1)(g-1) - P_m f^2 \right].
$$
\n(19)

The thermodynamic critical field follows

$$
H_c = \sqrt{8\pi F_c} = \left\{ 32\pi^3 N(0) T_{c0}^2 \right\}^{1/2} U(t), \tag{20}
$$

where

$$
U(t) = \left\{ t \sum_{n=0}^{\infty} [\delta f + t(2n+1)(g-1) - P_m f^2] \right\}^{1/2}.
$$
 (21)

Hence, we have the dimensionless thermodynamic field:

$$
h_c = \frac{H_c \hbar^2 v^2}{2\pi \phi_0 T_{c0}^2} = \frac{\hbar^2 v^2}{\phi_0 T_{c0}} \sqrt{8\pi N(0)} U(t). \tag{22}
$$

The prefactor by *U*, which is a characteristic of the clean material, can be expressed in terms of the GL parameter  $\kappa_0$  for the clean limit [\[21\]](#page-5-0):

$$
\kappa_0 = \frac{3\phi_0 T_{c0}}{\hbar^2 v^2 \sqrt{7\zeta(3)\pi N(0)}}.
$$
\n(23)

Thus, we obtain

$$
h_c(t, P_m) = \frac{3}{\kappa_0} \sqrt{\frac{8}{7\zeta(3)}} U(t, P_m).
$$
 (24)

To evaluate the condensation energy in Eq. (19), one first must find  $f$  and  $\delta$  for given  $t$  and  $P_m$ . For the uniform zerofield state, these are solutions of the Eilenberger equation for *f* and of the self-consistency equation. In our notation, this system of two equations for  $f(t, P_m)$  and  $\delta(t, P_m)$  reads

$$
\sqrt{1 - f^2} (\delta - P_m f) - t \left( n + \frac{1}{2} \right) f = 0, \tag{25}
$$

$$
-\delta \ln t = \sum_{n=0}^{\infty} \left( \frac{\delta}{n + \frac{1}{2}} - tf \right). \tag{26}
$$

The system can be solved numerically with the help of Wolfram Mathematica or MATLAB. Evaluation of  $h_c(t, P_m)$  is then straightforward.

Results for  $h_c$  and  $h_{c2}$  are shown in the left panel of Fig. 3 for the clean case. For the parameter  $\kappa = 0.5$ , we have type-I behavior, while type II is realized for  $\kappa = 1$  and 2, as expected since the boundary value is  $\kappa_0 = 1/\sqrt{2} \approx 0.7$ . The effect of pair-breaking scattering is nontrivial; to see this, we show the case of exclusively pair-breaking scattering, in which for both  $\kappa = 0.5$  and 1, the material behaves as type I since  $h_c > h_{c2}$ .

One may say that pair-breaking scattering pushes materials toward type I, the conclusion we arrived at in Ref. [\[22\]](#page-5-0) in a different manner.

#### **IV. SUMMARY**

We have studied the effects of transport and pair-breaking scattering on the upper critical field  $H_{c2}$ , the thermodynamic critical field  $H_c$ , and the nucleation field  $H_c$ <sub>3</sub> of surface superconductivity for the field parallel to the plane surface of the half-space isotropic sample. We did not touch on questions of



FIG. 3. *Hc* (thin dashed lines) for the indicated values of the Ginzburg-Landau parameter  $\kappa_0$  and  $H_{c2}$  (thick red line) in units  $2\pi \phi_0 T_{c0}^2 / \hbar^2 v^2$  vs  $T/T_{c0}$ . (a) Clean case  $P = P_m = 0$ . (b) Strong magnetic scattering  $P_m = 0.1$ , in the absence of potential scattering  $P = 0$ . When a dashed blue line is above the solid red line, the material is a type-I superconductor.

surface roughness, surface curvature, inhomogeneous distribution of impurities [\[5\]](#page-5-0), material anisotropy [\[12\]](#page-5-0), etc.

Whereas  $H_{c2}$  is suppressed by pair-breaking scattering,  $H<sub>c3</sub>$  is found to be suppressed as well so that the ratio  $\mathcal{R} =$  $H_{c3}/H_{c2}$  is within the window  $1.55 \lesssim R \lesssim 2.34$  regardless of temperature or magnetic or nonmagnetic scattering. We find that the magnetic impurities do not qualitatively change the behavior of the ratio  $R$  with changing temperature and transport scattering:  $\mathcal{R}(T)$  is equal to the SJDG value 1.695 at *Tc* but increases on cooling, goes through a maximum at intermediate temperatures, and then drops to a *P*-dependent value at  $T = 0$  [\[13\]](#page-5-0). The addition of magnetic impurities does not change this qualitative behavior, the suppression of the critical temperature notwithstanding.

The thermodynamic critical field  $H_c$  along with the condensation energy is also suppressed by pair-breaking scattering, but depending on material parameters and temperature, the speed of this suppression could be larger or smaller than that of  $H_{c2}$ . On the other hand, the value of  $H_c$  relative to  $H_{c2}$  is crucial for the type of emerging superconductivity: type I for  $H_c > H_{c2}$  and type II for  $H_c < H_{c2}$ . A possibility of changing the type of material superconductivity by changing the concentration of magnetic impurities has also been discussed in Ref. [\[22\]](#page-5-0).

The summary of our results for the critical fields at a low temperature is given in Fig. [4.](#page-4-0)

Using our routine of calculating the condensation energy, we looked at the phase transition between gapped and gapless superconductivity; the question recently attracted the attention of the community. We found that the third derivative of the free energy with respect to the pair-breaking parameter has a singular discontinuous jump at  $T = 0$  predicted in Refs. [\[23,24\]](#page-5-0). The transition, however, broadens at finite *T* , see Appendix [B.](#page-4-0)

We mention yet another example of the second-order phase transition that can be treated within the same formal scheme as  $H<sub>c3</sub>$ . This is the problem of nucleation of superconductivity in thin films in a parallel applied field [\[19\]](#page-5-0). The boundary condition  $\nabla_n \Delta(\mathbf{r}) = 0$  should now be obeyed at both film

<span id="page-4-0"></span>

FIG. 4. The summary of our results for  $H_{c2}(P, P_m)$  (top left),  $H_{c3}(P, P_m)$  (top right),  $\mathcal{R}(P, P_m) = H_{c3}(P, P_m) / H_{c2}(P, P_m)$  (lower left), and the ratio  $H_{c2}(P, P_m)/H_c(P, P_m)$  (lower right) at the same reduced temperature  $T/T_c(P_m) = 0.1$ . All fields are in units of  $2\pi\phi_0 T_{c0}^2/\hbar^2 v^2$ .

surfaces, and the emerging state, being physically like that of the surface superconductivity of SJDG, can even be nucleated at  $T > T_c$  at a nonzero magnetic field. The  $T_c(H)$  enhancement in this geometry had been observed [\[25,26\]](#page-5-0), but a careful investigation of this intriguing possibility is still to be done. Finally, we are unaware of experimental studies of  $H_{c3}$  in superconducting materials with magnetic impurities. Perhaps, this paper will motivate further research.

#### **ACKNOWLEDGMENTS**

The authors are grateful to James Sauls, Alex Levchenko, and Alex Gurevich for helpful discussions. This paper was supported by the U.S. DOE, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. DE-AC02-07CH11358. RP acknowledges support by the DOE National Quantum Information Science Research Centers, Superconducting Quantum Materials and Systems Center under Contract No. DE-AC02- 07CH11359.

## **APPENDIX A: THE SUM** *S* **IN THE PRESENCE OF MAGNETIC IMPURITIES**

The solution  $f$  of Eq. [\(1\)](#page-0-0) can be written as

$$
f = (2\omega^+ + \mathbf{v}\mathbf{\Pi})^{-1} \left(\frac{F}{\tau^-} + 2\Delta\right)
$$
  
= 
$$
\int_0^\infty d\rho \exp[-\rho(2\omega^+ + \mathbf{v}\mathbf{\Pi})] \left(\frac{F}{\tau^-} + 2\Delta\right).
$$
 (A1)

Here,  $F = \langle f \rangle$ . Taking the Fermi surface average, we get

$$
F = \frac{1}{\tau^{-}} \int_0^{\infty} d\rho \exp(-2\omega^+ \rho) \langle \exp(-\rho \mathbf{v} \mathbf{\Pi}) \rangle (F + 2\Delta \tau^{-}).
$$
\n(A2)

The term  $\langle \ldots \rangle$  does not contain the scattering parameters; hence, it is the same as that calculated in Ref. [\[18\]](#page-5-0) for the clean case:

$$
\langle \exp(-\rho \mathbf{v} \Pi) \tilde{F} \rangle
$$
  
=  $\sum_{m,j} \frac{(-q^2)^j}{(m!)^2 j!} \frac{(2\mu)!!}{(2\mu+1)!!} \left(\frac{\rho v}{2}\right)^{2\mu} (\Pi^+)^m (\Pi^-)^m \tilde{F}$ . (A3)

Here,  $\tilde{F} = F + 2\Delta \tau^{-}$ ,  $\mu = m + j$ , and  $\Pi^{\pm} = \Pi_x \pm i\Pi_y$ . After integrating over  $\rho$ , one obtains from Eq. (A2)

$$
F = \frac{1}{2\omega^{+}\tau^{-}} \sum_{m,j} \frac{(-q^{2})^{j}}{j!(2\mu+1)} \left(\frac{\mu!}{m!}\right)^{2} \left(\frac{\ell^{+}}{\beta^{+}}\right)^{2\mu}
$$

$$
\times (\Pi^{+})^{m} (\Pi^{-})^{m} \tilde{F},
$$

$$
\ell^{+} = v\tau^{+}, \quad \beta^{+} = 1 + 2\omega\tau^{+}.
$$
 (A4)

One can check that, if no magnetic impurities are involved, this reduces to Eq.  $(12)$  of Ref. [\[18\]](#page-5-0). Using commutation properties of operators  $\Pi^{\pm}$  in the uniform field, one manipulates

$$
(\Pi^+)^m (\Pi^-)^m \tilde{F} = \tilde{F} \prod_{i=1}^m [k^2 + (2i - 1)q^2]
$$
 (A5)

and obtains

$$
F = \Delta \frac{2\tau^{-}S}{2\omega^+ \tau^- - S},
$$
  
\n
$$
S = \sum_{m,j} \frac{(-q^2)^j}{j!(2\mu + 1)} \left(\frac{\mu!}{m!}\right)^2 \left(\frac{\ell^+}{\beta^+}\right)^{2\mu}
$$
  
\n
$$
\times \prod_{i=1}^m [k^2 + (2i - 1)q^2].
$$
 (A6)

## **APPENDIX B: CONDENSATION ENERGY VS PAIR-BREAKING PARAMETER** *Pm*

Recently, the character of the quantum phase transition between gapped and gapless superconductivity at  $T = 0$  [\[24\]](#page-5-0) when the pair-breaking scattering parameter *Pm* varies through the value  $\exp(-\pi/4 - \gamma)/2 = 0.128$  (see, e.g., Ref. [\[16\]](#page-5-0)). Remarkably, It turned out that the superconducting density of states as function of energy  $\omega$  and of the order parameter  $\Delta(P_m)$  undergoes a topological transition at  $P_m = 0.128$ . In the Ehrenfest classification, the transition can be considered of the 2.5th order, at which the third derivative of the free energy ∂<sup>3</sup>*Fc*/∂*P*<sup>3</sup> *<sup>m</sup>* is singular.

Although this question is out of the scope of the main subject of this paper, we utilize here the functionals in Eqs.  $(16)$ and [\(17\)](#page-2-0) and the condensation energy  $F_c(T, P_m)$  of Eq. [\(18\)](#page-2-0) <span id="page-5-0"></span>derived above and valid for any *T* and any scattering parameters  $P, P_m$ .

One should mention that solving a coupled system of Eqs.  $(25)$  and  $(26)$  is not a trivial task. The lower the temperature, the more Matsubara summations are required. Initially, calculations were conducted with the help of Wolfram Mathematica; however, it could not handle the lowest temperatures. Final calculations were performed within MATLAB that still required at least 100 000 summations to obtain the reported results (interested readers are welcome to contact the authors for further technical details).

As can be seen in Fig. 5, temperature affects the behavior of the third derivative of the condensation energy dramatically when compared with the exact result at  $T = 0$  obtained using Eq. (71) from Maki's review [20]. Our calculations confirm the existence of a very sharp discontinuity of  $\partial^3 F_c(T, P_m)/\partial P_m^3$  at  $T \to 0$  at  $P_m = 0.128$  (or at  $\zeta = \hbar/\Delta \tau_m = (2\pi T_{c0}/\Delta)P_m = 1$  in notations of Ref. [23]). However, we were unable to confirm the claim that the discontinuity is preserved at nonzero temperatures [23]; our calculation shows that the singularity in  $F_c'''(P_m)$  broadens with increasing *T*. In fact, at finite temperatures, the singularity disappears while its trace moves to lower scattering rates  $P_m$ . As expected, this confirms that the critical magnetic scattering rate for a transition to the gapless state decreases starting from  $P_m = 0.128$  at  $T = 0$  to lower values at higher temperatures [27].

- [1] A. Gurevich, [Rev. Accl. Sci. Tech.](https://doi.org/10.1142/S1793626812300058) **05**, 119 (2012).
- [2] D. B. Liarte, S. Posen, M. K. Transtrum, G. Catelani, M. Liepe, and J. P. Sethna, [Supercond. Sci. Technol.](https://doi.org/10.1088/1361-6668/30/3/033002) **30**, 033002 (2017).
- [3] M. H. Devoret and R. J. Schoelkopf, Science **339**[, 1169 \(2013\).](https://doi.org/10.1126/science.1231930)
- [4] C. Rigetti, J. M. Gambetta, S. Poletto, B. L. T. Plourde, J. M. Chow, A. D. Córcoles, J. A. Smolin, S. T. Merkel, J. R. Rozen, G. A. Keefe *et al.*, Phys. Rev. B **86**[, 100506\(R\) \(2012\).](https://doi.org/10.1103/PhysRevB.86.100506)
- [5] [V. Ngampruetikorn and J. A. Sauls,](https://doi.org/10.1103/PhysRevResearch.1.012015) Phys. Rev. Research **1**, 012015(R) (2019).
- [6] D. Saint-James and P. G. De Gennes, Phys. Lett. **7**[, 306 \(1963\).](https://doi.org/10.1016/0031-9163(63)90047-7)
- [7] D. Saint-James, G. Sarma, E. J. Thomas, *Type II Superconductivity* (Pergamon, Oxford, New York, 1969).
- [8] P.-G. de Gennes, *Superconductivity of Metals and Alloys* (Advanced Book Program, Perseus Books, Reading, Mass.,1999).
- [9] [W. J. Tomasch and A. S. Joseph,](https://doi.org/10.1103/PhysRevLett.12.148) Phys. Rev. Lett. **12**, 148 (1964).
- [10] C. F. Hempstead and Y. B. Kim, [Phys. Rev. Lett.](https://doi.org/10.1103/PhysRevLett.12.145) **12**, 145 (1964).
- [11] [M. Strongin, A. Paskin, O. F. Kammerer, and M. Garber,](https://doi.org/10.1103/PhysRevLett.14.362) *Phys.* Rev. Lett. **14**, 362 (1965).
- [12] V. G. Kogan, J. R. Clem, J. M. Deang, and M. D. Gunzburger, Phys. Rev. B **65**[, 094514 \(2002\).](https://doi.org/10.1103/PhysRevB.65.094514)
- [13] [H.-Y. Xie, V. G. Kogan, M. Khodas, and A. Levchenko,](https://doi.org/10.1103/PhysRevB.96.104516) *Phys.* Rev. B **96**, 104516 (2017).



FIG. 5. The third derivative of the free energy at a set of low temperatures  $t = T/T_{c0} = 0.05, 0.03, 10^{-2}, 10^{-3},$  and  $5 \times 10^{-5}$  vs the pair-breaking parameter  $\zeta = \hbar / \Delta \tau_m = (2\pi T_{c0}/\Delta) P_m$ . In addition, the curve at  $T = 0$  obtained using the exact Eq. (71) from Maki's review [20].  $\zeta = 1$  and  $P_m = 0.128$  correspond to the transition to the gapless state at  $T = 0$ . In this calculation, the sum over *n* was extended up to  $N_{\text{max}} = 10^5$ .

- [14] [V. G. Kogan and R. Prozorov,](https://doi.org/10.1103/PhysRevB.90.180502) Phys. Rev. B **90**, 180502(R) (2014).
- [15] G. Eilenberger, Z. Phys. **214**[, 195 \(1968\).](https://doi.org/10.1007/BF01379803)
- [16] [V. G. Kogan, R. Prozorov, and V. Mishra,](https://doi.org/10.1103/PhysRevB.88.224508) Phys. Rev. B **88**, 224508 (2013).
- [17] E. Helfand and N. R. Werthamer, Phys. Rev. **147**[, 288 \(1966\).](https://doi.org/10.1103/PhysRev.147.288)
- [18] V. G. Kogan, [Phys. Rev. B](https://doi.org/10.1103/PhysRevB.32.139) **32**, 139 (1985).
- [19] V. G. Kogan and N. Nakagawa, Phys. Rev. B **35**[, 1700 \(1987\).](https://doi.org/10.1103/PhysRevB.35.1700)
- [20] K. Maki, in *Superconductivity*, edited by R. D. Parks, Vol. 2 (Marcel Dekker, New York, 1969).
- [21] A. Fetter and P. C. Hohenberg, in *Superconductivity*, edited by R. D. Parks, Vol. 2 (Marcel Dekker, New York, 1969).
- [22] V. G. Kogan and R. Prozorov, Phys. Rev. B **88**[, 024503 \(2013\).](https://doi.org/10.1103/PhysRevB.88.024503)
- [23] [Y. Yerin, A. A. Varlamov, and C. Petrillo,](https://doi.org/10.1209/0295-5075/ac64b9) Europhys. Lett. **138**, 16005 (2022).
- [24] [Y. Yerin, C. Petrillo, and A. A. Varlamov,](https://doi.org/10.21468/SciPostPhysCore.5.1.009) Sci. Post Core. **5**, 009 (2022).
- [25] H. Jeffrey Gardner, A. Kumar, L. Yu, P. Xiong, M. P. [Warusawithana, L. Wang, O. Vafek, and D. G. Schlom,](https://doi.org/10.1038/nphys2075) Nat. Phys. **7**, 895 (2011).
- [26] Y. Ma, J. Pan, C. Guo, X. Zhang, L. Wang, T. Hu, G. Mu, F. Huang, and Xiaoming Xie, [npj Quant. Mater.](https://doi.org/10.1038/s41535-018-0107-2) **3**, 34 (2018).
- [27] V. Ambegaokar and A. Griffin, Phys. Rev. **137**[, A1151 \(1965\).](https://doi.org/10.1103/PhysRev.137.A1151)