Entropy and Spin Susceptibility of $s$-wave Type-II Superconductors near $H_{c2}$

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A theoretical study is performed on the entropy $S_n$ and the spin susceptibility $\chi_s$ near the upper critical field $H_{c2}$ of $s$-wave type-II superconductors with arbitrary impurity concentrations. The changes of these quantities through $H_{c2}$ may be expressed as

$$\frac{S_n(T, B) - S_n(T, 0)}{S_n(T) - S_n(T, 0)} = 1 - \alpha_S \left( 1 - \frac{B}{H_{c2}} \right)^{\alpha_S} \quad \text{and} \quad \frac{\chi_s(T, B) - \chi_s(T, 0)}{\chi_s(T) - \chi_s(T, 0)} = 1 - \alpha \chi \left( 1 - \frac{B}{H_{c2}} \right)^{\alpha \chi},$$

where $\alpha_S$ and $\alpha$ are exponents determined by the zero-energy density of states, and vary from 1.72 in the dirty limit to 0.5 to 0.6 in the clean limit. This mean-free-path dependence of $\alpha_S$ and $\alpha$ at $T = 0$ is quantitatively the same as that of the slope $S_n(T = 0)$ for the flux-flow resistivity studied previously. The result suggests that $S_n(B)$ and $\chi_s(B)$ near $T = 0$ are convex downward (upward) in the dirty (clean) limit, deviating substantially from the linear behavior $\alpha B/H_{c2}$. The specific-heat jump at $H_{c2}$ also shows fairly large mean-free-path dependence.

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I. INTRODUCTION

This paper considers the changes of the entropy $S_n$ and the spin susceptibility $\chi_s$ through $H_{c2}$ for classic $s$-wave type-II superconductors. These quantities were calculated by Maki in the dirty limit for superconducting alloys nearly 40 years ago. However, detailed studies on clean systems are still missing even for $s$-wave superconductors. Writing these quantities as

$$S_n(T, B) = S_n(T, 0) - \gamma_n S_n(T, 0), \quad \chi_s(T, B) = \chi_s(T, 0) - \gamma_s \chi_s(T, 0),$$

the slopes $\gamma_n$ and $\gamma$ will be obtained quantitatively for arbitrary impurity concentrations. The results near $H_{c2}$ will also be useful for getting an insight into the behaviors over $0 \leq B \leq H_{c2}$. Indeed, $\alpha > 1$ ($\alpha < 1$) indicates overall field dependence which is convex downward (upward), as realized from Eq. (1).

It seems to have been widely accepted that various physical quantities of classic $s$-wave type-II superconductors follow the linear field dependence with $\alpha = 1$ at low temperatures. A theoretical basis for it is the density of states for a single vortex calculated by Caroli, de Gennes, and Matricon. However, few quantitative calculations have been carried out so far on the explicit field dependence. Recently, Ichioka et al. performed a numerical study on the density of states of clean two-dimensional $s$-wave superconductors with $\kappa > 1$ at $T = 0.5T_c$. They found the exponent $\alpha = 0.67$ for the overall field dependence of the zero-energy density of states. Also, experiments on the $T$-linear specific-heat coefficient $\gamma_n(B)$ for clean V$_3$Si $^{10}$ and NbSe$_2$ $^{11,12}$ show marked upward deviations from the linear behavior $\gamma_n(B)/H_{c2}$. Even early experiments on $\gamma_n(B)$ for clean V and Nb indicate similar deviations $^{12,13}$ although not recognized explicitly in those days due to the absence of a theory on clean systems. These results indicate that the field dependence with $\alpha < 1$ is a general feature of clean $s$-wave superconductors, as suggested by Ramirez.$^{9}$

Following the preceding works on the Maki parameters$^{14}$ and the flux-flow resistivity$^{15}$ which will be referred to as I and II, respectively, I present a detailed study on $S_n$ and $\chi_s$ near $H_{c2}$ at all temperatures. I thereby hope to clarify the $\kappa$ and mean-free-path ($l_{tr}$) dependence of $\alpha_S$ and $\alpha$. Calculations are performed for both two and three dimensional isotropic systems to see the dependence of $\alpha_S$ and $\alpha$ on detailed Fermi-surface structures. I also calculate the specific heat jump at $H_{c2}$ for various values of $\kappa$ and $l_{tr}$. To my knowledge, this kind of a systematic study has not been performed even for classic $s$-wave superconductors.

Unlike the convention, I adopt the average flux density $B$ in the bulk as an independent variable instead of the external field $H$. An advantage for it is that the irrelevant region $H \leq H_{c1}$ is automatically removed from the discussion on the field dependence. This distinction between $B$ and $H$ becomes important for low-$\kappa$ materials where $H_{c2} < H_{c1}$ occupies a substantial part of $0 \leq H \leq H_{c2}$. Any experiment on the $B$ dependence should be accompanied by a careful measurement on the magnetization, especially for low-$\kappa$ materials like Nb and V.

Section II provides the formulation, Sec. III presents numerical results, and Sec. IV summarizes the paper. I put $k_B = 1$ throughout.

II. FORMULATION

A. Entropy and Pauli paramagnetism

As before$^{14,15}$ I consider the $s$-wave pairing with an isotropic Fermi surface and $s$-wave impurity scattering in an external magnetic field $H \parallel z$. The formulation
proceeds in exactly the same way for both the three-dimensional system and the two-dimensional system placed in the $xy$ plane perpendicular to $H$. The vector potential in the bulk can be written as \( A(r) = B x \hat{y} + \hat{A}(r) \),

\[
A(r) = B x \hat{y} + \hat{A}(r), 
\]

where $B$ is the average flux density produced jointly by the external current and the supercurrent inside the sample, and $\hat{A}$ expresses the spatially varying part of the magnetic field satisfying \( \int \nabla \times \hat{A} \, dr = 0 \).

I first write down the expressions of the entropy and the magnetization in the presence of Pauli paramagnetism. As can be checked directly, the effect can be included in the Eilenberger equations for the quasiclassical Green’s functions $f$, $f^\dagger$, and $g$ by the replacement:

\[
\varepsilon_n \rightarrow \varepsilon'_n = \varepsilon_n - i \mu_B \hat{z} \cdot (\nabla \times \hat{A}),
\]

where $\varepsilon_n \equiv (2n+1) \pi T$ is the Matsubara energy and $\mu_B$ is the Bohr magneton. The corresponding Eilenberger functional for the free-energy difference between the normal and superconducting states is given by

\[
F = \int dr \left\{ \frac{(\nabla \times \hat{A})^2}{8 \pi} + N(0) |\Delta(r)|^2 \ln \frac{T}{T_c} \right. \\
+ \pi T N(0) \sum_{n=-\infty}^{\infty} \frac{|\Delta(r)|^2}{|\varepsilon_n|} - \langle I(\varepsilon_n, k_F, r) \rangle \left\}.
\]

Here $\Delta$ is the order parameter, $N(0)$ is the density of states per spin and per unit volume at the Fermi level, $k_F$ is the Fermi wavevector, and $\langle \cdots \rangle$ denotes Fermi-surface average satisfying $\langle 1 \rangle = 1$. The quantity $I$ is defined by

\[
I = \Delta^* f + \Delta f^\dagger + 2 \varepsilon'_n [g - \text{sgn}(\varepsilon_n)] + \frac{f(f^\dagger) + (f^\dagger)f}{4 \tau} + \frac{g(g^\dagger) - 1}{2 \tau} - \frac{f^\dagger v_F \cdot \partial f - f v_F \cdot \partial^* f^\dagger}{2 |g + \text{sgn}(\varepsilon_n)|},
\]

where $\tau$ is the relaxation time in the second-Born approximation, $v_F$ is the Fermi velocity, and $\partial$ denotes

\[
\partial \equiv \nabla - \frac{i e}{\hbar c} \hat{A}.
\]

The quasiclassical Green’s functions $f$ and $g$ are connected by $g = (1 - f f^\dagger)^{1/2} \text{sgn}(\varepsilon_n)$ with $f^\dagger(\varepsilon_n, k_F, r; \mu_B) = f^\dagger(\varepsilon_n, -k_F, r; -\mu_B)$. The change of sign in $\mu_B$ is necessary here, because $f \equiv f_{\uparrow \downarrow} \neq f_{\downarrow \uparrow}$ in the presence of Pauli paramagnetism. The functional derivatives of Eq. (4) with respect to $f^\dagger$, $\Delta^*$, and $\hat{A}$ lead to the Eilenberger equation for $f$, the self-consistency equation for $\Delta(r)$, and the Maxwell equation for $\hat{A}$, respectively.

The expression of the entropy $S_n$ is obtained from Eq. (4) by the thermodynamic relation: $S_n = S_n - \partial F/\partial T$. Considering the stationarity with respect to $f$, $\Delta$, and $\hat{A}$, we only have to differentiate with respect to the explicit temperature dependence in $F$. We thereby obtain

\[
S_n = S_n - \frac{N(0)}{T} \int dr \left[ |\Delta(r)|^2 - \pi T \sum_{n=-\infty}^{\infty} \langle I(\varepsilon_n, k_F, r) \rangle - 2 \pi T \sum_{n=-\infty}^{\infty} \varepsilon_n (g - \text{sgn}(\varepsilon_n)) \right],
\]

where $S_n = 2 \pi^2 N(0) V T^3 / 3$ with $V$ the volume of the system. In contrast, the expression of the external field $H$ may be derived by applying the Doria-Gubernatis-Rainer scaling to Eq. (4). The details are given in Appendix A of I, and we obtain

\[
H = -4 \pi M_{np} + B + \frac{1}{BV} \int dr (\nabla \times \hat{A})^2 \\
+ \frac{\pi^2 TN(0)}{BV} \sum_{n=-\infty}^{\infty} \int dr \left( \frac{\hbar^2 v_F \cdot \partial f - f v_F \cdot \partial^* f^\dagger}{g + \text{sgn}(\varepsilon_n)} \right) \\
+ i \frac{8 \pi^2 TN(0) \mu_B}{BV} \sum_{n=-\infty}^{\infty} \int dr <g> \hat{z} \cdot (\nabla \times \hat{A}),
\]

where $M_{np} = 2 \mu_B^2 N(0) B$ denotes the normal-state magnetization due to Pauli paramagnetism. We thus arrive at the expression of the magnetization from Pauli paramagnetism as

\[
M_{np} = M_{np} - \frac{2 \pi TN(0) \mu_B}{BV} \sum_{n=-\infty}^{\infty} \int dr <g> \hat{z} \cdot (\nabla \times \hat{A}).
\]

When Pauli paramagnetism is negligible compared with the orbital diamagnetism by supercurrent, we can take the limit $\mu_B \to 0$ in Eqs. (4) and (5) and retain only the leading-order terms. This results in $\varepsilon'_n \to \varepsilon_n$ for Eq. (4). On the other hand, Eq. (4) is transformed by noting Eq. (5) into

\[
M_{sp} = M_{np} \left[ 1 - \frac{\pi T}{V} \sum_{n=-\infty}^{\infty} \int dr \frac{\partial <g>}{\partial \varepsilon_n} \frac{(\nabla \times \hat{A})^2}{B^2} \right].
\]

If the zero-field expression $g = \varepsilon_n / \sqrt{\varepsilon_n^2 + |\Delta|^2}$ is substituted into Eq. (10) with $\nabla \times \hat{A} = B \hat{z}$, the terms in the square bracket reduces to the Yosida function.

### B. Expressions near $H_{c2}$

I now consider the cases where Pauli paramagnetism is small and provide explicit expressions to Eqs. (4) and (5) near $H_{c2}$. From now on I adopt the units used previously, where the energy, the length, and the magnetic field are measured by the zero-temperature energy gap $\Delta(0)$ at $H = 0$, the coherence length $\xi_0 \equiv h v_F / \Delta(0)$ with $v_F$ the Fermi velocity, and $B_0 \equiv \phi_0 / 2 \pi \xi_0^2$ with $\phi_0 \equiv hc/2\pi$ the flux quantum, respectively, with $h=1$. 
First, $f, g,$ and $\tilde{A}$ are expanded up to the second order in $\Delta(r)$ as

\[
\begin{align*}
    f &= f^{(1)} \quad g = (1 - \frac{1}{2}f^{(1)}f^{(1)}) \operatorname{sgn}(\varepsilon_n) \quad \text{(11)} \\
    \tilde{A} &= \tilde{A}^{(2)}
\end{align*}
\]

Substituting them into Eqs. (7) and (10) and using the Eilenberger equations for $f^{(1)}$ and $f^{(1)}$ to remove terms with $v_F \cdot \nabla$, we obtain

\[
\frac{S_n}{S_n} = 1 - \frac{3}{2\pi T^2} \int dr \left[ |\Delta(r)|^2 - \frac{\pi T}{2} \sum_n (f^{(1)}f^{(1)} + f^{(1)}\Delta^* + \pi T \sum_n |\varepsilon_n| (f^{(1)}f^{(1)}) \right], \tag{12a}
\]

\[
\frac{M_p}{M_n^p} = 1 + \frac{\pi T}{2\pi} \sum_n \int dr \left[ \frac{\partial f^{(1)}}{\partial \varepsilon_n} f^{(1)} + f^{(1)} + \frac{\partial f^{(1)}}{\partial \varepsilon_n} \right] \operatorname{sgn}(\varepsilon_n). \tag{12b}
\]

Further, $\Delta(r)$ and $f^{(1)}$ near $H_c2$ can be expanded in the basis functions $\psi_{Nq}(r)$ of the vortex lattice as

\[
\Delta(r) = \sqrt{V} \Delta_0 \psi_{0q}(r), \tag{13a}
\]

\[
f^{(1)}(\varepsilon_n, r_F, r) = \sqrt{V} \Delta_0 \sum_{N=0}^{\infty} \tilde{f}_N(\varepsilon_n, \theta) e^{iN\varphi} \psi_{Nq}(r), \tag{13b}
\]

where $(\theta, \varphi)$ are the polar angles of $r_F$ with $\sin \theta \to 1$ in two dimensions, $N$ denotes the Landau level, and $q$ is an arbitrary chosen magnetic Bloch vector characterizing the broken translational symmetry of the flux-line lattice and specifying the core locations. The coefficients $\Delta_0$ and $\tilde{f}_N$ are both real for the relevant hexagonal lattice. Substituting these expressions into Eqs. (12a) and (12b) and using the orthonormality of $\psi_{Nq}(r)$ and $e^{iN\varphi}$, we obtain

\[
\frac{S_n}{S_n} = 1 - \frac{3\Delta_0^2}{2\pi T^2} \int dr \left[ 1 - \pi T \sum_{n=-\infty}^{\infty} \langle \tilde{f}_0^{(1)} \rangle \right] + \pi T \sum_{n=-\infty}^{\infty} |\varepsilon_n| \sum_{N=0}^{\infty} (-1)^N \langle \tilde{f}_N^{(1)} \tilde{f}_N^{(1)} \rangle, \tag{14a}
\]

\[
\frac{M_p}{M_n^p} = 1 + \pi T \Delta_0^2 \sum_{n=-\infty}^{\infty} \sum_{N=0}^{\infty} (-1)^N \langle \frac{\partial \tilde{f}_N^{(1)}}{\partial \varepsilon_n} \tilde{f}_N^{(1)} \rangle \operatorname{sgn}(\varepsilon_n). \tag{14b}
\]

Except $\Delta_0^2 \propto H_c2 - B$, all the quantities in Eqs. (14a) and (14b) are to be evaluated at $H_c2$.

It is possible to give an alternative expression to Eq. (14a) using the equation for $H_c2$ given by Eq. (33) of I:

\[
\ln \frac{T_c}{T} + \pi T \sum_{n=-\infty}^{\infty} \left[ \langle \tilde{f}_0^{(1)}(\varepsilon_n) \rangle - \frac{1}{|\varepsilon_n|} \right] = 0. \tag{15}
\]

Differentiating Eq. (15) with respect to $T$ yields

\[
-1 + \pi T \sum_{n=-\infty}^{\infty} \left[ \langle \tilde{f}_0^{(1)} \rangle + \frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial \varepsilon_n} \varepsilon_n + \frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial H_c2} \frac{dH_c2}{dT} \right] = 0. \tag{16}
\]

The quantity $\partial \langle \tilde{f}_0^{(1)} \rangle / \partial H_c2$ has been calculated as Eqs. (31)-(32) of I to be

\[
\frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial H_c2} = \sum N (-1)^{N+1} \sqrt{\frac{N+1}{8H_c2}} \langle \tilde{f}_N^{(1)} \tilde{f}_N^{(1)} \sin \theta \rangle. \tag{17}
\]

A similar procedure enables us to obtain the expressions of $\partial \langle \tilde{f}_0^{(1)} \rangle / \partial \varepsilon_n$ and $\tilde{f}_N^{(1)} / \partial \varepsilon_n$ in Eq. (14a) as

\[
\frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial \varepsilon_n} = - \sum N (-1)^N \langle \tilde{f}_N^{(1)} \tilde{f}_N^{(1)} \rangle \operatorname{sgn}(\varepsilon_n), \tag{18a}
\]

\[
\frac{\partial \tilde{f}_N^{(1)}}{\partial \varepsilon_n} = - \sum N K_N^{\prime} \langle \tilde{f}_N^{(1)} \rangle + \frac{K_0}{2\pi} \operatorname{sgn}(\varepsilon_n) \frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial \varepsilon_n}, \tag{18b}
\]

where $K_N^{\prime}$ is defined by Eq. (25) of I. Using Eqs. (10) and (18a) in Eq. (14a), we obtain

\[
\frac{S_n}{S_n} = 1 - \frac{dH_c2}{dT} \frac{3\Delta_0^2}{2\pi} \sum_{n=-\infty}^{\infty} \langle \tilde{f}_N^{(1)}(\varepsilon_n) \rangle, \tag{19}
\]

with

\[
\frac{dH_c2}{dT} = \frac{1 - \pi T \sum_{n=-\infty}^{\infty} \langle \tilde{f}_0^{(1)} \rangle + \frac{\partial \langle \tilde{f}_0^{(1)} \rangle}{\partial \varepsilon_n} \varepsilon_n}{\pi T^2 \sum_{n=-\infty}^{\infty} \langle \frac{\partial \tilde{f}_0^{(1)}}{\partial H_c2} \rangle}. \tag{20}
\]

Using Eq. (20) we can also calculate the specific-heat jump at $H_c2$. It is given in conventional units as

\[
\Delta C = \frac{T}{4\pi} \left( \frac{dH_c2}{dT} \right)^2 \frac{1}{(2k_\beta - 1)\beta_A}, \tag{21}
\]

where $k_\beta$ is the Maki parameter and $\beta_A = 1.16$.

Equations (14) and (21) with Eqs. (17), (13), and (20) are the main analytic results of the paper. The quantities $\Delta_0$, $\tilde{f}_N^{(1)}$, and $k_\beta$ have been obtained in I. The explicit expression of $\tilde{f}_N^{(1)}$ is given by

\[
\tilde{f}_N^{(1)} = \frac{\tilde{K}_N^{\prime} \operatorname{sgn}(\varepsilon_n)}{1 - (\tilde{K}_0^{\prime})\operatorname{sgn}(\varepsilon_n)/2\pi}, \tag{22}
\]

where $K_N^{\prime}$ may be calculated efficiently by the procedure in Sec. IIF of I, with a change of definition of $\varepsilon_n$ as

\[
\tilde{\varepsilon}_n \equiv \left[ |\varepsilon_n| + \frac{1}{2\pi} \right] \operatorname{sgn}(\varepsilon_n). \tag{23}
\]
C. Analytic results at $T = 0$

Now it will be shown that Eqs. (14a) and (14b) reduce to an identical expression at $T = 0$ for arbitrary impurity concentrations, which has the physical meaning of the zero-energy density of states.

Let us start from Eq. (14a) where $\varepsilon_n > 0$ and $\varepsilon_n < 0$ yield the same contribution. Using this fact and Eq. (15a), it is transformed into

$$
\frac{S_s}{S_n} = 1 - \frac{3\Delta_0^2}{2\pi^2 T^2} \left[ 1 - 2\pi T \sum_{n=0}^{\infty} \left( \frac{\tilde{f}_0^{(1)}(\varepsilon_n)}{\varepsilon_n} + \frac{\partial \tilde{f}_0^{(1)}(\varepsilon_n)}{\partial \varepsilon_n} \right) \right].
$$

The summation over $n$ for $T \to 0$ may be performed by using the Euler-Maclaurin formula and the asymptotic property $\tilde{f}_0^{(1)}(\varepsilon_n) \to \varepsilon_n^{-1} (\varepsilon_n \to \infty)$.

For example,

$$
2\pi T \sum_{n=0}^{\infty} \left( \frac{\tilde{f}_0^{(1)}(\varepsilon_n)}{\varepsilon_n} \right) \approx \int_{-\infty}^{\infty} \left( \frac{\tilde{f}_0^{(1)}(\varepsilon)}{\varepsilon} \right) d\varepsilon + \pi T \left( \frac{\tilde{f}_0^{(1)}(\varepsilon)}{\varepsilon} \right) \left( \pi T \right) - \frac{(\pi T)^2}{6} \left( \frac{\tilde{f}_0^{(1)}(\varepsilon)}{\varepsilon} \right) \left( \pi T \right).
$$

We thereby obtain

$$
\frac{S_s}{S_n} \to 0 \quad 1 + \Delta_0^2 \left( \frac{\tilde{f}_0^{(1)}(\varepsilon_n)}{\varepsilon_n^2} \right).
$$

Equation (14b) may be transformed similarly as

$$
M_{dp} \to \frac{M_{dp}}{M_{np}} = 1 - \pi T \Delta_0^2 \sum_{n=0}^{\infty} \frac{\partial^2 \tilde{f}_0^{(1)}(\varepsilon_n)}{\partial \varepsilon_n^2} \left( \frac{\tilde{f}_0^{(1)}(\varepsilon_n)}{\varepsilon_n} \right).$$

Thus, $S_s / S_n = M_{dp} / M_{np}$, or equivalently, $\alpha_s = \alpha_x$ at $T = 0$ for arbitrary impurity concentrations.

Equations (26a) and (26b) have a simple physical meaning. Indeed, noting Eq. (13a), (15b), and Eq. (15a), we find an alternative expression at $T = 0$:

$$
\frac{S_s}{S_n} = \frac{M_{dp}}{M_{np}} = \frac{1}{V} \int \langle g(\varepsilon_n = 0, k_F, \varepsilon) \rangle d\varepsilon,
$$

which is nothing but the normalized density of states at $\varepsilon = 0$. Thus, we have arrived at a simple result that the entropy and spin susceptibility at $T = 0$ are both determined by the zero-energy density of states.

The coefficient of $\Delta_0^2 \propto H_{c2} - B$ have been obtained in I. Also, $\tilde{f}_0^{(1)}(0)$ in Eqs. (26a) and (26b) may be calculated efficiently from Eq. (22) by using the analytic expression $\tilde{f}_0^{(1)}(0)$.

$$
\tilde{K}_0^{(1)}(\varepsilon_n, \beta) = \sqrt{2} \int_0^{\infty} \frac{\tilde{\varepsilon}_n}{\tilde{\varepsilon}_n + \frac{\beta^2}{2}} e^{-\frac{\beta^2}{2}} dx,
$$

with $\beta \equiv \sqrt{H_{c2} \sin \theta / 2\sqrt{2}}$. Hence, Eqs. (26a) and (26b) at $T = 0$ can be evaluated fairly easily.

D. Analytic results in the dirty limit

I here summarize analytic results in the dirty limit $\tau \to 0$. First, the key quantities $K_0^0$ are calculated by choosing $N_{cut} = 1$ in the procedure in Sec. IIF of I. The results are given by

$$
\tilde{K}_0^{(0)} = \frac{\tilde{\varepsilon}_n}{\tilde{\varepsilon}_n + \frac{\beta^2}{2}}, \quad \tilde{K}_0^{(1)} = \frac{\beta}{\tilde{\varepsilon}_n + \frac{\beta^2}{2}}.
$$

Since $\beta^2$ is of the order of $1/\tau$, as shown below, $\langle \tilde{K}_0^{(0)} \rangle$ may be approximated as $\langle \tilde{K}_0^{(0)} \rangle \approx 1/(\tilde{\varepsilon}_n - \beta^2 / \tilde{\varepsilon}_n) \approx \tilde{\varepsilon}_n / (\tilde{\varepsilon}_n^2 + \beta^2)$. Using this $\langle \tilde{K}_0^{(0)} \rangle$ in Eq. (22) and retaining only the leading-order contributions, we obtain

$$
\tilde{f}_0^{(1)} = \frac{1}{|\tilde{\varepsilon}_n| + 2\tau \beta^2}, \quad \tilde{f}_1^{(1)} = \frac{2\tau \beta \text{sgn}(\tilde{\varepsilon}_n)}{|\tilde{\varepsilon}_n| + 2\tau \beta^2}.
$$

Notice that $\tilde{f}_0^{(1)}$ is smaller than $\tilde{f}_0^{(1)}$ by $\sqrt{\tau}$. Substitution of Eq. (30) into Eq. (15) leads to the equation for $H_{c2}$ obtained by Maki and de Gennes:

$$
\ln(T_c/T) + \psi(1/2) - \psi(x) = 0,
$$

where $\psi$ is the digamma function, and $x$ is defined by

$$
x = \frac{1}{2} + \frac{\tau \beta^2}{\pi T} = \frac{1}{2} + \frac{\tau H_{c2}}{4\pi T d}.
$$

with $d = 2, 3$ dimension of the system. As shown by Maki and de Gennes Eq. (31) can be solved near $T = 0$ by using the asymptotic expression of $\psi(x)$ as

$$
H_{c2} \approx \frac{d}{\tau} \left[ 1 - \frac{2}{3} (\pi T)^2 \right].
$$

Thus $\beta^2 \propto H_{c2} \sim \tau^{-1}$, as assumed at the beginning. Differentiating Eq. (31) with respect to $T$, we obtain

$$
\frac{dH_{c2}}{dT} = \frac{H_{c2}}{T} \left[ 1 - \frac{4\pi T d}{\tau H_{c2} \psi'(x)} \right].
$$

Finally, $\kappa_2$ and $[\Delta_0(B)^2]$ are calculated from Eqs. (34b) and (36) of I as

$$
\kappa_2 = \frac{d\sqrt{-\psi(2)(x)}}{2\sqrt{2\pi T d} \psi'(x)} \left( \frac{H_{c2} - B}{\Delta_0^2} \right)^{1/2} \left( \frac{H_{c2} - B}{H_{c2}} \right)^{1/2},
$$

$$
\Delta_0^2 = \frac{(H_{c2} - B)\kappa_0^2}{2\kappa_0^2 - 1} \frac{4\pi T d}{\psi'(x)} \left( \frac{H_{c2} - B}{H_{c2}} \right)^{1/2} \left( \frac{H_{c2} - B}{H_{c2}} \right)^{1/2}.
$$

where $\kappa_0$ is defined by $\kappa_0 \equiv \phi_0/(2\pi \xi_0^2 H_{c2}(0))$ with $H_{c2}(0)$ the thermodynamic critical field at $T = 0$. Equation (32) agrees with the result by Caroli, Cylot, and de Gennes.

Now, let us substitute Eq. (31) into Eqs. (14a) and (15) and use Eqs. (33). We thereby obtain

$$
\frac{S_s}{S_n} = 1 + \frac{dH_{c2}}{dT} \frac{3\pi \Delta_0^2}{8\pi^2 T d} \psi'(x) \left( \frac{H_{c2} - B}{H_{c2}} \right)^{1/2} - 2\Delta_0^2.
$$
Thus, \( M_{sp}/M_{np} \) and \( S_{c}/S_{n} \) is the same at \( T = 0 \), in agreement with Eq. \( (27) \); they are both determined by the zero-energy density of states. Equation \( (37b) \) is the result obtained by Maki. Also, the expression \( 1 - 2\Delta_{0}^{2} \) for the normalized zero-energy density of states at \( T = 0 \) agrees with the result for the local density of states obtained by de Gennes.\(^{4,27}\) Equation \( (38) \) tells us that \( \Delta_{0}^{2} = (1 - B/H_{c2})\beta_{A}^{-1} \) as \( T \to 0 \) for \( \kappa_{2} \gg 1 \). We hence find from Eqs. \( (1), \ (37a), \) and \( (37b) \) that the initial slopes at \( T = 0 \) for \( \kappa_{2} \gg 1 \) are given by

\[ \alpha_{S} = \alpha_{\chi} = 2/\beta_{A} = 1.72. \]  

The results suggest the overall field dependence of \( S_{c} \) and \( \chi_{s} \) at \( T = 0 \) which is convex downward. Notice that the flux-flow resistivity \( \rho_{f} \) at \( T = 0 \) also has the same initial slope \( \alpha_{f} = 1.72 \) in the dirty limit.\(^{15,29,30}\) These results strongly suggest that the density of states at \( \varepsilon = 0 \) is mainly relevant to the physical properties of the vortex state at \( T = 0 \).

### E. The case with p-wave impurity scattering

If the p-wave impurity scattering is relevant, the following additional terms appears on the right-hand side of Eq. \( (4) \):

\[ \frac{d}{4\tau_{1}} \left( \langle \mathbf{k}' \mathbf{f} \rangle + \langle \mathbf{k}' \cdot \mathbf{f} \rangle \right) + \frac{d}{2\tau_{1}} \langle \mathbf{k} \cdot \mathbf{g} \rangle, \]  

where \( \langle \mathbf{k}' \mathbf{g} \rangle \equiv \langle \mathbf{k}' \mathbf{g}(\mathbf{n}, \mathbf{k}_{p}, \mathbf{r}) \rangle \), for example, \( \tau_{1} \) is the p-wave relaxation time, and \( \mathbf{k} \) is the unit vector along \( \mathbf{k}_{p} \). However, Eqs. \( (14) \) and \( (21) \) are also valid together with Eqs. \( (17), \ (18), \) and \( (20) \), where \( \tilde{f}_{N}^{(1)} \) is now given by

\[ \tilde{f}_{N}^{(1)} = \frac{1}{D} \left\{ \left[ 1 - \frac{d}{4\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] \langle \mathbf{k}_{p} \rangle \right\} + \frac{1}{2\tau_{1}} \langle \mathbf{k} \rangle \mathbf{g} \sin \theta \left[ \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right]. \]  

with

\[ D \equiv \left[ 1 - \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] \langle \mathbf{k}_{p} \rangle \left[ 1 - \frac{d}{4\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] + \frac{d}{8\tau_{1}} \langle \mathbf{k}_{p} \rangle \sin \theta \left[ \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] \sin \theta \left[ \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right]. \]  

In addition, Eq. \( (18d) \) is to be replaced by

\[ \frac{\partial \tilde{f}_{N}^{(1)}}{\partial \varepsilon_{n}} = - \sum_{N} \tilde{K}_{N}^{0} \frac{\partial \tilde{f}_{N}^{(1)}}{\partial \varepsilon_{n}} + \frac{K_{N}^{0} \sin \theta}{2\tau_{1}} \frac{\partial \tilde{f}_{N}^{(1)}}{\partial \varepsilon_{n}} \sin \theta, \]  

where

\[ \frac{\partial \tilde{f}_{N}^{(1)} \sin \theta}{\partial \varepsilon_{n}} = - \sum_{N} \left( -1 \right)^{N} \langle \tilde{f}_{N}^{(1)} \rangle \sin \theta \sin \theta \]  

with

\[ \frac{\partial \tilde{f}_{N}^{(1)} \sin \theta}{\partial \varepsilon_{n}} = \frac{1}{\tau_{1}} \left\{ \left[ 1 - \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] \langle \mathbf{k}_{p} \rangle \right\} \left[ 1 - \frac{1}{2\tau_{1}} \langle \mathbf{k}_{p} \rangle \right] \sin \theta \]  

Finally, the analytic results in the dirty limit are the same as those given in Sec. IID with a replacement of \( \tau \) by the transport life time \( \tau_{tr} \) defined through

\[ \frac{1}{\tau_{tr}} = \frac{1}{\tau} - \frac{1}{\tau}. \]  

### F. Numerical procedures

I have adopted the same parameters as I and II to express different impurity concentrations:

\[ \xi_{E}/l_{tr} \equiv 1/2\pi T_{c} \tau_{tr}, \quad l_{tr}/l \equiv \pi \tau_{tr}/\tau. \]  

Numerical calculations of Eqs. \( (14), \ (15), \) and \( (21) \) with Eqs. \( (17), \ (18), \) and \( (20) \) have been performed for each set of parameters by restricting every summation over the Matsubara frequencies for those satisfying \( |\varepsilon_{n}| \leq \varepsilon_{c} \). Choosing \( \varepsilon_{c} = 200 \) is sufficient to obtain an accuracy of \( \sim 0.1\% \) for Eqs. \( (14), \ (15), \) and \( (21) \), whereas \( \varepsilon_{c} = 20000 \) (4000) is required for Eq. \( (15a) \) in the dirty (clean) limit. Summations over Landau levels have been truncated at \( N = N_{cut} \), where I put \( R_{N_{cut}} = 1 \) in the calculation of \( \tilde{K}_{N}^{0} \); see Sec. IIF of I for the details. Enough convergence has been obtained by choosing \( N_{cut} = 4, 10, 100, 200, 1500, \) and 4000 for \( \xi_{E}/l_{tr} = 50, 1.0, 0.5, 0.1, \) and 0.05, respectively. Finally, integrations over \( \theta \) have been performed by Simpson’s formula with \( N_{cut} + 1 \) integration points for \( 0 \leq \theta \leq \pi/2 \).

### III. RESULTS

Figures \( (1) \) and \( (2) \) show temperature dependence of \( \alpha_{S} \) and \( \alpha_{\chi} \) defined by Eqs. \( (15) \) and \( (16) \), respectively, for different impurity concentrations parametrized by Eq. \( (10) \). They have been calculated in three dimensions for \( l_{tr}/l = 1.0 \) and \( \kappa_{GL} = 50 \). All the curves start from the
same value $\alpha_S = \alpha_\chi = 0.862$ at $T = T_c$ and develop differences among different impurity concentrations at lower temperatures. The equality $\alpha_S = \alpha_\chi$ holds at $T = 0$, as shown by Eq. (27), and the value decreases from 1.72 in the dirty limit to around 0.6 for $\xi_l / l_t = 0.1$. According to Eq. (27), this variation in the slope at $T = 0$ can be attributed to the dependence of the zero-energy density of states $N_n(0, B)$ upon the impurity concentration. In particular, $N_n(0, B)$ in the dirty (clean) limit decreases more rapidly (mildly) than the linear behavior $N_n(0) B / H_c2$ near $H_c2$. From this result, we expect the overall field dependence of the entropy and spin susceptibility at $T = 0$ which is convex downward (upward) in the dirty (clean) limit, as realized from Eq. (1).

The difference between $\alpha_S$ and $\alpha_\chi$ at finite temperatures is rather small, as expected from $\alpha_S = \alpha_\chi$ holding at $T = 0$ and $T_c$. In particular, the curves of $\alpha_S$ and $\alpha_\chi$ in the dirty limit depend neither on the dimensions nor $l_t / l$. However, the dependence develop gradually as the mean free path becomes longer.

Figure 3 shows the slope $\alpha(0) = \alpha_S(0) = \alpha_\chi(0)$ as a function of $\xi_l / l_t$ for $d = 2, 3$, $l_t / l = 1, 2$, and $\kappa_{GL} = 50$. We thus realize that the zero-energy density of states is mainly determined by the mean free path, and does not depend much on the dimensions nor the details of the impurity scattering.

It is interesting to note that the slope $\alpha_f$ for the flux-flow resistivity $\rho_f$, which was calculated previously for $d = 2, 3$, $l_t / l = 1, 0$, and $\kappa_{GL} = 50$, show a complete numerical agreement at $T = 0$ with the corresponding $\alpha_S$ and $\alpha_\chi$, i.e., $\alpha_S = \alpha_\chi = \alpha_f$ for arbitrary impurity concentrations at $T = 0$. This fact indicates that $\rho_f$ at $T = 0$ is also determined by the zero-energy density of states.

Next, we examine the dependence of the slopes on the Ginzburg-Landau parameter $\kappa_{GL}$. Figure 4 shows the same curves as Fig. 1 near the type-I-type-II boundary of $\kappa_{GL} = 1$. Each curve is shifted upwards from the corresponding one in Fig. 1 for $\kappa_{GL} = 50$, but the quantitative difference is rather small. This is also the case for $\alpha_\chi$. Thus, the slopes $\alpha_S$ and $\alpha_\chi$ as a function of $B$ do not have large $\kappa_{GL}$ dependence.

Finally, Fig. 5 plots the specific-heat jump $\Delta C$ over $T$ at $H_{c2}$ as a function of $T / T_c$ for different impurity concentrations with $d = 3$, $l_t / l = 1.0$, and $\kappa_{GL} = 1$. We note that the overall behavior of $\Delta C / T$ over $T / T_c$ is the same as a function of $\xi_l / l_t$. This fact indicates that $\Delta C / T$ over $T / T_c$ does not depend on the impurity concentration $d$ and $\kappa_{GL}$.
concentrations with $d = 3$, $l_{tr}/l = 1$, and $\kappa_{GL} = 50$. It is normalized by the corresponding quantity at $T = T_c$ and $H = 0$, i.e., $\Delta C(T_c)/T_c = 1.43$ in the weak-coupling model. The curves change gradually from almost $T$-linear at lowest temperatures. Although the ratio $\kappa_{GL}$ is strongly dependent on $\kappa_{GL}$, the basic features pointed above are common among different values of $\kappa_{GL}$; $d = 2, 3$, and $l_{tr}/l = 1, 2$.

IV. SUMMARY

The entropy and the spin susceptibility near $H_{c2}$ have been calculated for $s$-wave type-II superconductors over all impurity concentrations. The results have been expressed conveniently using the initial slopes $\alpha_s$ and $\alpha_\chi$ defined by Eq. (1). The main conclusions are summarized as follows: (i) $\alpha_s = \alpha_\chi$ holds both at $T = 0$ and $T = T_c$. (ii) $\alpha_s = \alpha_\chi = 0.862$ at $T = T_c$ for all impurity concentrations. (iii) At $T = 0$, the slope $\alpha$ decreases from $1.72$ in the dirty limit to $0.5 \sim 0.6$ in the clean limit. This change is due to the mean-free-path dependence of the zero-energy density of states. The fact also suggests variation of the overall field dependence at $T = 0$ from convex downward in the dirty limit to upward in the clean limit. (iv) The slopes have only small dependence on the dimensions and the details of the impurity scattering. (v) The slope $\alpha_e$ of the flux-flow resistivity $\rho_f$, which was calculated previously also shows a complete numerical agreement at $T = 0$ with $\alpha_s$ and $\alpha_\chi$. This fact indicates that the zero-energy density of states is also responsible for $\rho_f$ at $T = 0$.

The $T$-linear specific-heat coefficient $\gamma_e(B)$ observed in clean materials show curves of $\alpha < 1$, which are in a qualitative agreement with the present calculation. On the other hand, $\gamma_e(B)$ for dirty samples follows well-accepted linear field dependence $\propto B/H_{c2}$, which is apparently in contradiction with the present result in the dirty limit. It should be noted however that a careful experiment on $\rho_f$ shows field dependence near $T = 0$ which is convex downward, and experimentally obtained $\alpha_e$ agrees quantitatively with the dirty-limit theory. Detailed experiments on the mean-free-path dependence of $\gamma_e(B)$ and $\rho_f(B)$ are desired to remove these discrepancies.

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