Curie law, entropy excess, and superconductivity in heavy fermion metals and other strongly interacting Fermi liquids

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Low-temperature thermodynamic properties of strongly interacting Fermi liquids with fermion condensate are investigated. We demonstrate that the spin susceptibility of these systems exhibits the Curie-Weiss law, and the entropy contains a temperature-independent term. The excessive entropy is released at the superconducting transition, enhancing the specific heat jump \( \Delta C \) and rendering it proportional to the effective Curie constant. The theoretical results are favorably compared with the experimental data on the heavy fermion metal CeCoIn\(_5\), as well as \(^3\)He films.

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Theoretical understanding of strongly interacting Fermi systems, such as heavy-fermion metals, is challenging. Conventionally, electrons in solids are classified as either itinerant or localized. The former have a Fermi surface, and their spin susceptibility \( \chi \) at low temperature \( T \) follows the Pauli law \( \chi(T) = \text{const} \), whereas the latter exhibit the Curie law \( \chi \propto 1/T \). The Curie law is observed in many heavy-fermion metals \(^2\)\(^6\)\(^{11}\) and is commonly attributed to the localized character of the \( f \) electrons. However, in some of these materials, such as CeCoIn\(_5\) \(^4\)\(^5\) and PuCoGa\(_5\) \(^6\)\(^7\), the low-temperature Curie law is immediately followed by a superconducting transition, also associated with the \( f \) electrons \(^8\). If the \( f \) electrons are localized, how can they superconduct? Actually, measurements of the Fermi surfaces of the heavy fermion metals by magnetic oscillations directly demonstrate that the \( f \) electrons are itinerant, in agreement with band structure calculations \(^8\). However, if the \( f \) electrons are itinerant, how can they exhibit the low-temperature Curie law?

We show that these puzzles can be resolved within the Fermi-liquid theory if itinerant electrons form the so-called “fermion condensate” state \(^1\)\(^2\)\(^{11}\). The interplay between band-like and atomic-like behavior of electrons in solids is often treated on the basis of the Hubbard model and the dynamical mean-field theory \(^11\). Heavy fermions are typically described by the Anderson-Kondo lattice models of coupled itinerant and localized electrons originating from different orbitals, sometimes using the two-fluid description \(^12\). However, given the experimental evidence that the \( f \) electrons are itinerant in some heavy-fermions metals, here we study a conceptually simpler model where all electrons are itinerant. Our goal is not to present a detailed, material-specific description, but to illustrate general ideas also applicable to other puzzling Fermi systems, such as \(^3\)He films \(^12\)\(^14\).

Let us consider a system of itinerant electron quasiparticles characterized by dispersion \( \varepsilon_p \), where \( \varepsilon \) is energy measured from the chemical potential, and \( p \) is momentum. The spin susceptibility \( \chi_0 \) per one electron is

\[
\chi_0 = -\mu_e^2 \int \frac{dn(\varepsilon_p)}{d\varepsilon_p} \, dp = \frac{\mu_e^2}{T} \int n(p) [1 - n(p)] \, dp,
\]

where \( dp = 2d^3p/(2\pi)^3 \) is the volume element in 3D momentum space, \( \rho \) is the electron concentration, and \( \mu_e \) is the magnetic moment of electron in solid. In a simple case, \( \mu_e \) is equal to the Bohr magneton \( \mu_B \), but, for heavy fermions, \( \mu_e \) may also contain a contribution from the orbital angular momentum, as discussed later in the paper. The occupation numbers \( n(p) \) are given by the Fermi distribution function

\[
n(p) = [1 + \exp(\varepsilon_p/T)]^{-1}
\]

where the Boltzmann constant \( k_B \) is set to 1. In ordinary Fermi liquids, \( \varepsilon_p \approx v_F(p-p_F) \), where \( v_F \) is the Fermi momentum, and \( v_F \) is the Fermi velocity. In this case, the integral in Eq. (1) is proportional to \( T \), and \( \chi_0(T) = \mu_e^2 N_0/\rho = \text{const} \), where \( N_0 = p_F^3/\pi^2v_F \) is the density of states at the Fermi level. Accounting for the spin-spin interaction amplitude \( g_0 \) modifies Eq. (1) via the Stoner factor: \( \chi = \chi_0/(1 - g_0\chi_0) \).

The quasiparticle dispersion \( \varepsilon_p \) is affected by the Landau interaction function \( f_L(p,p') = \delta\varepsilon_p/\delta n(p') \). In general, \( f_L(p,p') \) is a functional of the occupation numbers \( n(p) \), but here, for the sake of illustration, we take \( f_L(p,p') \) as a given function. Then, \( \varepsilon_p \) is related to the bare dispersion \( \varepsilon_p^0 \) as

\[
\varepsilon_p = \varepsilon_p^0 + \int f_L(p,p') \, n(p') \, dp' .
\]

The dispersion \( \varepsilon_p \) and the occupation numbers \( n(p) \) are obtained by solving Eqs. (2) and (3) self-consistently. When the interaction \( f_L \) is weak, Eq. (3) merely renormalizes the Fermi velocity. However, when the interaction strength exceeds a critical value, the minimum of the total energy at \( T = 0 \) may be achieved in a radically different state with the fermion-condensate state. In
this state, the quasiparticle spectrum is completely flat \( \varepsilon_p = 0 \) at \( T = 0 \) in some region of momentum space, where the occupation function \( n_\ast(p) \) continuously interpolates between 0 and 1 [3]. The increase of kinetic energy in this state is compensated by the decrease of interaction energy. Nozières [10] demonstrated that, at low \( T \neq 0 \), the momentum occupation function remains the same \( n(p) = n_\ast(p) \) in the domain occupied by the fermion condensate. Thus, the self-consistent dispersion \( \varepsilon_p \) becomes temperature-dependent

\[
\varepsilon_p = T \ln \left( \frac{1 - n_\ast(p)}{n_\ast(p)} \right),
\]

as follows from the inversion of Eq. (2). The group velocity \( \partial \varepsilon_p / \partial p \) in Eq. (4) is proportional to \( T \), which generates a sharp peak in the density of states with the velocity proportional to \( 1/T \) and results in unusual thermodynamic properties discussed below. Measurements of magnetic oscillations in the heavy-fermion metals indeed show enormous flattening of \( \varepsilon_p \) relative to the band-structure calculations [3].

This qualitative analysis has been confirmed by analytical and numerical solutions of Eqs. (2) and (3) for various interaction functions \( f_L \). As an example, in Fig. 4 we show \( n(p) \) and \( \varepsilon_p \) numerically calculated for three different temperatures for a toy model with an isotropic parabolic dispersion, characterized by the bare mass \( m \) and the bare Fermi energy \( \varepsilon_0^F = p_F^2/2m \). The interaction function \( f_L(q) \), where \( q = p - p' \), was chosen to be \( f_L(q) = \lambda / \{ [1 - (q/2p_F)^2 + \beta^2] \} \) with \( \beta = 0.48 \) and \( \lambda = 3p_Fm/\pi^2 \). Panel (a) shows that \( n(p) \) markedly differs from a step function and does not depend on temperature in the interval \([p_1, p_2]\). Panel (b) demonstrates that \( \varepsilon_p \) changes with \( T \), but the inset shows that the ratio \( \varepsilon_p / T \) is \( T \)-independent in the interval \([p_1, p_2]\), in agreement with Eq. (5). Fig. 4 illustrates that a self-consistent solution of quite conventional equations (2) and (3) for a rather generic, non-singular interaction function does generate the fermion condensate. Similar results were found for other isotropic and crystal lattice models, where \( p \) is quasimomentum in the Brillouin zone: see Ref. [12] and references therein. The results are robust and do not depend significantly on model details. Although the toy model utilized for the calculations shown in Fig. 4 is not necessarily realistic for specific materials, the fermion condensate formation is a generic process, and only the fermion condensate parameters, not the model details, matter for observable quantities.

Now let us discuss observable manifestations of the fermion-condensate state in detail. Substituting the temperature-independent occupation function \( n_\ast(p) \) of the fermion condensate into Eq. (4), we find a Curie contribution to the spin susceptibility [10]

\[
\chi_0 = \frac{\kappa \mu^2}{T} + \chi(T), \quad \kappa = \int_{p_1}^{p_2} n_\ast(p) \left[ 1 - n_\ast(p) \right] dp, \quad (5)
\]
even though all electrons are itinerant. The effective Curie constant in Eq. (5) is reduced by the dimensionless parameter \( \kappa \) relative to the Curie law \( \chi_0 = \mu^2 / T \) of a non-degenerate Fermi gas at high temperatures \( T > \varepsilon_0^F \).

The second term \( \chi \) in Eq. (4) comes from integration outside of the fermion-condensate domain \([p_1, p_2]\) in Eq. (4). This term is less singular than the Curie term, which dominates at low \( T \). Accounting for the spin interaction amplitude \( g_0 \) generates the Curie-Weiss law \( \chi(T) \approx \mu^2 / (T - \Theta_W) \) with the Weiss temperature \( \Theta_W = g_0 \mu^2 \). The numerically calculated \( \chi_0(T) \) for the same model as in Fig. 4 is shown by the solid line in Fig. 2b. The finite value of the product \( \chi_0(T) \) in the limit \( T \to 0 \) indicates the Curie behavior at low temperatures and gives the value \( \kappa \approx 0.1 \) in this model. In a wide temperature range, \( \chi_0(T) \) shown in Fig. 2b does not strictly follow the Curie law because of \( \chi(T) \).

In \( ^3\text{He} \) films, the low-\( T \) Curie constant is about 4 time lower than the high-\( T \) one, as shown in Fig. 1 of Ref. [15], which gives \( \kappa \approx 0.25 \) in this case. To evaluate \( \kappa \) for the heavy fermion metals from Eq. (5), we need to know the magnetic moment \( \mu \) of \( f \) electrons, which has spin and orbital contributions. In a free atom, \( \mu = g_L \mu_B \mathbf{J} \), where \( g_L \) is the Landé factor, and \( \mathbf{J} \) is the total angular momentum. The crystal field lifts degeneracy between energy levels with different projections \( J_z \) and causes magnetic anisotropy. In CeCoIn\(_5\), there

**FIG. 1:** Quasiparticle properties of a system with the fermion condensate, plotted vs. \( p/p_F \) for three temperatures \( T \): (a) the occupation numbers \( n(p) \), (b) the single-particle spectrum \( \varepsilon_p \) in the units of \( \varepsilon_0^F = p_F^2/2m \), (inset) the ratio \( \varepsilon_p / T \).
is one $f$-electron with $J = 5/2$, and the $c$ axis is the easy magnetic axis. Thus, the lowest energy levels have $J_z = \pm 5/2$, and the effective magnetic moment along the $c$ axis is $\mu = \mu_p g_L J_z = 2.14 \mu_B$, where $J_z = 5/2$ and $g_L = 0.857$ for $L = 3$, $S = 1/2$, and $J = 5/2$. As shown in Fig. 3 of Ref. 2, the low-$T$ Curie law in CeCoIn$_5$ is the most pronounced for the easy axis $c$ with the Curie constant $0.2\mu_B^2$. This value is much smaller than $\mu_p^2$, and we find from Eq. 3 that $\kappa = 0.2\mu_p^2/2.14\mu_B^2 = 0.044$.

The entropy $S$ per one particle for an ensemble of fermion quasiparticles is given by the formula

$$S = -\int \{ n(p) \ln n(p) + [1 - n(p)] \ln [1 - n(p)] \} \, dp. \quad (6)$$

In ordinary Fermi liquids, the integrand in Eq. (6) differs from zero only in a narrow vicinity of the Fermi surface, so $S = T\pi^2/6\nu_F p_F$ and $S \to 0$ when $T \to 0$. In contrast, in the fermion-condensate state with the occupation function $n_F(p)$, the integrand is nonzero in a finite region, so the entropy has a temperature-independent contribution $S_\ast$. Extrapolating the normal-state $S(T)$ from the inset in Fig. 2 of Ref. 4 to $T \to 0$, we estimate that $S_\ast \approx 0.1 \ln 2$ in CeCoIn$_5$. We see that $S_\ast$ is finite, but much smaller than $S_\nu$ expected for an ensemble of localized spins $1/2$. Because it is proportional to the momentum-space volume occupied by the fermion condensate, $S_\ast$ may depend on external parameters, such as pressure $P$, so that $\partial S_\ast/\partial P \neq 0$.

In ordinary Fermi liquids, the specific heat $C = T(\partial S/\partial T)$ is proportional to $T$. The straight line of slope $1/2$ in Fig. 2a shows $C/\pi^2$ and $\chi_0 T/3\mu_p^2$ vs. $T/\varepsilon_F^0$ for a Fermi gas. The fermion condensate does not contribute to the specific heat, because its entropy $S_\ast$ is $T$-independent. So, the main contribution to $C$ comes from the regions in momentum space where $\varepsilon_p$ lies between the fermion condensate and the regular dispersion (see Fig. 1). When the fermion-condensate domain is small, $\varepsilon_p$ has inflection points at $\varepsilon_p = 0$ and $\varepsilon_p = \varepsilon_p^0$ for $\varepsilon_p < 0$ and $(\varepsilon_p - \varepsilon_p^0)$ for $\varepsilon_p > 0$, which gives $C \propto T^{1/3}$ and $\chi \propto T^{-2/3}$.

The inset in Fig. 2a shows the numerically calculated $C(T)$ for the same model as in Fig. 1 which indeed exhibits a sublinear power law. Because the calculated $\chi_0 T$ and $C$ have different temperature dependences, the Sommerfeld-Wilson (SW) ratio $R_{SW}^0 = \pi^2 \chi_0 T / 3C\mu_p^2$ increases with decreasing $T$, as shown by the solid line in Fig. 2b, and observed in heavy fermions [13]. This is in contrast to ordinary Fermi liquids, where $R_{SW}^0 = 1$, as shown by the horizontal line in Fig. 2b. Notice that the Stoner factor is not included in our definition of $R_{SW}^0$.

Although the excessive entropy $S_\ast$ of the fermion condensate does not contribute to the specific heat, it produces an enormous enhancement of the thermal expansion coefficient $\alpha = \partial V/\partial T \equiv -\partial S/\partial T$ and the Gruneisen ratio $\Gamma = \alpha/C$ [19]. In ordinary Fermi liquids, $S \propto T$, thus $\alpha \propto T$ vanishes at $T \to 0$, and $\Gamma(T) = const$. In contrast, for the fermion condensate, the derivative $\partial S_\ast/\partial T$ is $T$-independent, so $\alpha$ has a finite value at $T \to 0$. Experiment [20] shows that $\alpha$ is indeed temperature-independent at low $T$ and exceeds typical values for ordinary metals by the factor of $10^3$–$10^4$. With $\alpha \to const$ and $C(T) \to 0$, the Gruneisen ratio $\Gamma = \alpha/C$ diverges at low $T$, which is observed experimentally [21].

However, the existence of the residual entropy $S_\ast$ at $T \to 0$ contradicts the third law of thermodynamics (the Nernst theorem). To ensure that $S = 0$ at $T = 0$, localized spins order magnetically due to spin-spin interaction. Similarly, a system with the fermion condensate must experience some sort of a low-temperature phase transition eliminating the excessive entropy $S_\ast$. Here we focus on the second-order phase transition to a superconducting state [3]. The progressive increase of the fermion-condensate density of states with decreasing temperature facilitates superconducting instability in one of the pairing channels: $s$, $p$, $d$, etc. Elementary excitations in a superconductor are the Bogolyubov quasiparticles, whose spectrum $E_p = \sqrt{\varepsilon_p^2 + \Delta_p^2}$ has the energy gap $\Delta_p$. The entropy of a superconductor is given by Eq. 6 with $n(\varepsilon_p) \to f(E_p)$, where $f(E_p)$ are the occupation numbers of the Bogolyubov quasiparticles. Because of the energy gap, $f \to 0$, and so $S \to 0$ at $T \to 0$, thus the Nernst theorem is satisfied. However, in order to release

![FIG. 2: Thermodynamic properties of a fermion-condensate system.](image)
the excessive entropy $S_\ast$, the specific heat jump $\Delta C$ at the transition temperature $T_\ast$ is enhanced.

The specific heat $C_s$ of a superconductor is $C_s = \int dv_p E_p \, d(\alpha_p)/dT$. Taking the difference between $C_s$ and $C_n$, the specific heat in the normal state, we find the specific heat jump at $T_\ast$:

$$\Delta C = C_s - C_n = -\frac{1}{2T_\ast} \int \frac{\Delta^2}{dt} n(p) [1 - n(p)] \, dv_p.$$  \hspace{1cm} (7)

In the BCS theory, $\Delta^2/2T_c dT = -4\pi^2/T_\ast \zeta(3) \approx -4.7$, where $\zeta$ is the zeta function. (For $d$-wave pairing, the number is different, but the results do not change significantly.) Comparing Eqs. (1) and (7), we find

$$\Delta C = 4.7 T_\ast \chi_0/\mu^2 \equiv 1.43 C_n R_{SW}^{(0)}.$$ \hspace{1cm} (8)

Eq. (8) shows that the specific heat jump $\Delta C$ can be expressed in terms of either $\chi_0(T_c)$ or $C_n(T_c)$. For ordinary Fermi liquids, where the Sommerfeld-Wilson ratio $R_{SW}^{(0)} = 1$, Eq. (8) reproduces the familiar BCS relation $\Delta C/C_n = 1.43$. However, in the fermion condensate state, $R_{SW}^{(0)}$ changes with temperature, so $\Delta C/C_n$ does not have a universal value. Since $\chi_0 \propto 1/T$, the specific heat jump $\Delta C$ is not proportional to $T_\ast$, but is related to the fermion condensate parameter $\kappa$ in the Curie law \cite{23}.

$$\Delta C \approx 4.7 \kappa.$$ \hspace{1cm} (9)

Thus, the ratio $\Delta C/C_n$ can be very high when $T_\ast$ is low, because $C_n \to 0$ at $T \to 0$ while $\Delta C$ is finite.

Let us apply this analysis to CeCoIn$_5$, where $T_\ast = 2.3$ K. In this material \cite{22}, $\Delta C/C_n \approx 4.5$ is substantially higher than the BCS value, in agreement with our arguments. Using the value $\kappa \approx 0.044$ evaluated from the Curie law, we estimate the r.h.s. of Eq. (9) as 0.21. This is about a half of the experimental value of $\Delta C \approx 0.42$ per electron measured in Ref. \cite{22}. However, as shown in Fig. 3 of Ref. \cite{22}, the Curie term constitutes only about a half of the spin susceptibility at $T_\ast$. Thus, using the total susceptibility, we find that the relation \cite{22} between $\Delta C$ and $\chi_0$ is satisfied. In PuCoGa$_5$, we also attribute the Curie law, followed by a superconducting transition at $T_c = 18.5$ K \cite{22}, to the fermion condensate. However, quantitative estimate of $\kappa$ is difficult in this case, because plutonium has five $f$ electrons. Interestingly, if plutonium is replaced by uranium, the resulting material UC$_7$Ga$_5$ does not exhibit the Curie law and does not have superconducting transition \cite{22}. This is surprising from a conventional point of view, where “itinerant” electrons in UC$_7$Ga$_5$ should be more susceptible to superconducting pairing than “localized” electrons in PuCoGa$_5$. However, if the fermion condensate does not form in UC$_7$Ga$_5$, so that there is no Curie law, then the density of states is not enhanced, and superconductivity is not facilitated.

In conclusion, we have shown that strongly interacting Fermi liquids can form a fermion-condensate state, where quasiparticle dispersion $\varepsilon_p$ is flat at the Fermi level. Their magnetic susceptibility $\chi_0(T)$ exhibits the Curie-Weiss law with the effective Curie constant reduced by the fermion-condensate parameter $\kappa$. The entropy has the temperature-independent term $S_\ast$ (estimated as $S_\ast \approx 0.1$ in 2 per electron in CeCoIn$_5$), which greatly increases the thermal expansion coefficient $\alpha = -\partial S/\partial P$ at low $T$. The excessive entropy $S_\ast$ is released below the superconducting transition temperature $T_c$, which dramatically reduces $\alpha$ and enhances the specific heat jump $\Delta C/C_n$, as observed in CeCoIn$_5$ \cite{22,24}. The universal relation \cite{22} between $\Delta C$ and $T_c\chi_0(T_c)$ can be tested experimentally by checking whether the both quantities change proportionally upon variation of external parameters, such as pressure or chemical substitution \cite{22,24}.

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