The Chemical Potential and Thermodynamic Properties of Narrow-Band Superconductors

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Abstract. We discuss some of the consequences for the thermodynamic properties if a superconductor has a non-neglegible ratio of T_c/T_F. Starting from the BCS expression we derive an analytic expression for the thermodynamic potential at finite temperature, which has the relevant physical properties. From there we derive the corresponding Helmholtz-Ginzburg-Landau free energy functional near the phase transition, and discuss the behaviour of the order parameter, the chemical potential, the specific heat and the expansivity near T_c.

1. Introduction

One of the features that distinguishes 'exotic' [1] from ordinary superconductors is a relatively large scale of the transition temperature compared to the (still larger) Fermi temperature. This feature is sometimes used as an argument in favour of a Bose-Einstein condensation picture of high temperature superconductivity. From an analysis of the BCS model in the low density limit, it has been shown [2], that if T_c/T_F is no longer small, the chemical potential is shifted at $T = 0$. At finite temperature the shift of the chemical potential can be approximated by the relation $\mu(T)/\mu_n \simeq 1-|\Delta(T)/2\mu_n|^2$, where $\Delta(T)$ is the temperature dependent BCS-gap [3]. At the superconducting transition the first derivative of the chemical potential has a jump, given by the relation $\Delta(d\mu/dT)_{T_c} \approx 2.4T_c/T_F$. A qualitatively similar behaviour of μ has also been predicted for a two-dimensional (2D) charged boson gas, which undergoes pair condensation due to an attractive interaction between the bosons [4]. In 'classical' weak coupling and Migdal-Eliashberg theory this effect is not considered, because $T_c \ll T_F$ is assumed. The jump in the specific heat at T_c is calculated as $T\partial S/\partial T$ at fixed μ in the standard BCS treatment.
The anomaly in μ does not lead to unusual behaviour of the other thermodynamic functions. It merely causes a small reduction of the jump in the specific heat and the thermal expansivity coefficient. Only if T_c/T_F is of order 1 or larger this reduction would become noticable. On the other hand, if the electronic pressure is somehow externally fixed, a jump in $d\mu/dT$ implies a a jump in entropy (with a corresponding portion of latent heat at the phase transition), because μ is the Gibbs free energy per electron. However, as long as it is justified to assume that the volume is essentially constant due to the elastic restoring forces of the crystal, the electronic pressure is a temperature dependent quantity and the entropy has to be calculated either from the Helmholtz free energy or from the thermodynamic potential. Due to the large value of the bulk modulus (of order 100 GPa) compared to the superconductivity induced changes of electronic pressure ($\leq$ 60 kPa in high T_c cuprates), the changes of the crystal volume are indeed very small.

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2. General expressions for the thermodynamic potential and entropy of a BCS superconductor

We assume that the electrons interact with each other with an effective attraction V_{kq}, leading to a BCS-type superconducting state. The thermodynamic potential of a BCS superconductor is, after carrying out the Bogoliubov transformation [5]:

$$\begin{aligned}\Omega(\mu,T,V,\Delta) = & \sum_k \left[-2T\ln\left(1+e^{-E_k/T}\right)+\xi_k-E_k+\frac{\Delta_k^2}{E_k}\tanh\left(E_k/2T\right)\right] \\ & -\tfrac{1}{4}\sum_{kq}\left(\frac{\Delta_q}{E_q}\tanh\left(E_q/2T\right)\right)V_{kq}\left(\frac{\Delta_k}{E_k}\tanh\left(E_k/2T\right)\right) \quad ,\end{aligned} \tag{1}$$

where $E_k = \sqrt{\xi_k^2+\Delta_k^2}$ are the quasi-particle energies and $\xi_k = \epsilon_k - \mu$ are the single electron energies relative to the Fermi energy. The BCS gap equation can be obtained from this functional by looking for the minimum with respect to Δ_k. An expression for the average number of electrons is found from the relation $N_e = -\partial\Omega/\partial\mu$

$$\begin{aligned} 2 &= gW\sum_k \frac{\tanh\left(E_k/2T\right)}{E_k} \quad , \\ N_e &= \sum_k\left[1-\frac{\xi_k\tanh\left(E_k/2T\right)}{E_k}\right] \quad . \end{aligned} \tag{2}$$

The only types of excitations considered are the quasi-particles, hence the (fermionic) quasi-particle occupation numbers determine the electronic entropy in the usual way for a fermion gas, namely

$$S = -\frac{\partial}{\partial T}\Omega(\mu,T)\,|_\mu = -\sum_k\left[(1-f(E_k))\ln(1-f(E_k))+f(E_k)\ln f(E_k)\right] \quad . \tag{3}$$

The entropy depends on Δ and μ through the quasi-particle energies entering the Fermi occupation functions and through the integration boundaries. As these are analytical functions, and as we will see that Δ and μ have no discontinuity at T_c, also $S(T)$ is continuous at the phase transition. Hence the transition remains of the second order type.

3. Coupled gap equations of a layered superconducting electron gas

We assume that the electronic structure is represented by a stack of 2D layers, with a bandwidth $W = N_a/(V\rho)$, where V is the crystal volume, N_a is the number of atoms, and ρ is a constant density of states per unit volume. We assume that, in the same way as in a free electron model, ρ does not depend on V and N_a, and that the electrons have a k-independent non-retarded effective attractive interaction $(-gW)$, so that the gap-parameter Δ is also k-independent.
At $T = 0$ the thermodynamic potential is obtained by direct integration of Eq. 1. The summations over k can be replaced by integrals using the relation $\sum_k = V\rho\int_{-\mu}^{W-\mu} d\xi$

$$\Omega(\mu,0,V,\Delta) = -\rho V\left[\mu^2+\frac{\Delta^2}{2}\left(1+\frac{g}{2}\ln\frac{\Delta^2}{4W\mu}\left(\frac{2}{g}+\ln\frac{\Delta^2}{4W\mu}\right)\right)\right] \quad . \tag{4}$$

We determine Δ at the minimum, and the condition for particle number conservation as in the previous section. We furthermore approximate terms of the form $\ln\frac{4(W-\mu)\mu}{\Delta^2}$ with $\ln\frac{4W\mu}{\Delta^2}$, and expand in leading orders of Δ^2. This way we find

$$\Delta^2 = 4W\mu \exp\left(-\frac{2}{g}\right) \quad . \tag{5}$$

From direct integration of Eq. 2b, and after inserting the expression for Δ we find that the number of electrons tends to increase upon opening of the superconducting gap:

$$N_e = 2V\rho\left(\mu + \frac{\Delta^2}{4\mu}\right) \quad . \tag{6}$$

As the average number of electrons in a solid is macroscopically conserved due to the long range Coulomb forces, we now use this as a constraint on the chemical potential. Defining the Fermi temperature through the relation $N_e = 2V\rho\mu_n$ we obtain for the chemical potential

$$\mu = \frac{\mu_n}{2}\left(1 + \sqrt{1 - \frac{\Delta^2}{\mu_n^2}}\right) \simeq \mu_n - \frac{\Delta^2}{4\mu_n} \quad . \tag{7}$$

Because the change in μ is due to an increase of the surface charge, it is exactly matched by a change of workfunction ($\delta\mu + \delta W = 0$). Changes in workfunction manifest themselves as a modified electric field directly outside the sample surface, which can be measured with a variety of experimental techniques. Although the derivation leading to Eq. 7 is only valid at $T = 0$, from numerical calculations [3] it can be shown that the change in chemical potential due to the opening of a gap is given by the same relation if we insert $\Delta(T)$ for Δ. In the normal state $\mu_n(T)$ also depends on temperature due to the gradual transition to a non-degenerate gas at high temperatures. From Eqs. 5 and 6 we see that at the minimum with respect to Δ we have $\ln\frac{\Delta^2}{4W\mu} = -2/g$. Hence the expression for the Helmholtz free energy ($F(N_e, V) = \Omega(\mu, V) + 2\rho V\mu_n\mu$) for $T = 0$ is *at its minimum* with respect to Δ

$$F_s - F_n = -\frac{\rho V\Delta^2}{2}\left[1 + \frac{\Delta^2}{8\mu_n^2}\right] \quad . \tag{8}$$

4. Thermodynamic potential at finite temperature

For $T \neq 0$ it is not possible to solve the integrals occurring in the thermodynamic potential (Eq. 1) in closed analytical form. Instead we introduce a temperature dependance in a similar way as in the Ginzburg-Landau free energy. We first simplify the thermodynamic potential by realizing that in Eq. 4 the factor $\frac{g}{2}\ln\frac{\Delta^2}{4W\mu}$ occuring in front of the last two terms in brackets is almost constant and equal to -1 near the minimum. We approximate it with the constant value -1.

The first term of Eq. 1 equals $-\gamma T^2/2$ in the normal state. In the superconducting state it is reduced due to the opening of a gap. Using a series expansion for small T and Δ the leading terms are $-(\gamma T^2/2)(1 + \lambda\Delta^2(W^{-2} + \mu^{-2}))$, where λ is a dimensionless constant. The term proportional to Δ^2 adds a small contribution to the entropy, which we will however neglect in the rest of this discussion.

In the numerator inside the logarithmic term we replace Δ^2 with $\Delta^2 + \beta^2T^2$. From the various possible modifications leading to a temperature dependance this is the simplest one that leads correctly to a second order transition, with approximately the right temperature dependance of Δ, as well as various other properties in qualitative agreement with numerical calculations [3].

We furthermore define $D \equiv 4W\exp(-2/g)$, and combine the sum of three terms within the logarithm. We therefore consider the following form of Ω:

$$\Omega_s(\mu, T, V, \Delta) - (\Omega_n + \rho V\mu_n^2) = \rho V\left[-\mu^2 + \frac{\Delta^2}{2}\ln\frac{\Delta^2 + \beta^2T^2}{eD\mu}\right] \quad . \tag{9}$$

As we will later be interested in the electronic pressure, it is important to note in this context, that D is a volume dependent function, whereas β is a constant number.
The gap equation is obtained as usual from the minimum with respect to Δ. The number of electrons is found from $-\partial\Omega/\partial\mu$, which provides the temperature dependance of μ due to the opening of a gap. These coupled equations are

$$\begin{aligned} \Delta^2 &= \mu D \exp\left[\tfrac{\beta^2 T^2}{\Delta^2+\beta^2 T^2}\right] - \beta^2 T^2 \quad , \\ \tfrac{N_e}{\rho V} &= 2\mu_n = 2\mu + \tfrac{\Delta^2}{2\mu} \quad . \end{aligned} \tag{10}$$

At $T = 0$ these expressions are seen to reduce to the result of the previous section. From the equation for Δ we see, that the critical temperature is

$$T_c = \beta^{-1}\sqrt{eD\mu_n} \quad . \tag{11}$$

In order to have a $2\Delta_0/T_c$-ratio of about 3.5, we need $\beta \simeq 2.9$. The critical temperature depends on volume (and therefore on pressure) via D and μ_n. The latter is proportional to V^{-1}, whereas the volume dependance of the former can have any sign and value depending on the details of the underlying model [10]. The pressure dependance can be written in the form

$$\tfrac{d\ln T_c}{dp} = -\tfrac{1}{2B} + \tfrac{1}{2}\tfrac{d\ln D}{dp} \quad , \tag{12}$$

where B is the bulkmodulus of the crystal. Near the critical temperature we can expand around $\Delta = 0$:

$$\begin{aligned} \Delta(T)^2 &= \tfrac{\beta^2(T_c^2-T^2)}{2+eD/4\mu_n} \quad , \\ \mu &= \mu_n - \tfrac{\Delta(T)^2}{4\mu_n} + O(\Delta^4) \quad . \end{aligned} \tag{13}$$

5. Helmholtz free energy and thermodynamic properties

As we are interested in the thermodynamic properties of the system at constant particle number it is useful to write down the Helmholtz free energy. We can derive this quantity from the thermodynamic potential by means of a Legender transformation, *i.e.* by adding $\mu N_e = 2\mu\mu_n/\rho V$ and expressing all quantities which were previously a function of μ explicitly in the new variable N_e. For general values of Δ this requires the inversion of a rather formidable expression, but near T_c it is sufficient to make a Tayler series expansion of Δ, keeping only terms up to order Δ^4. The result is the following Ginzburg-Landau free energy functional

$$F_s(N_e,T,V,\Delta) - F_n = \rho V\left[\Delta^2 \ln\tfrac{T}{T_c} + \tfrac{\Delta^4}{2\beta^2 T_c^2}\left(1 + \tfrac{\beta^2 T_c^2}{8\mu_n^2}\right)\right] \quad , \tag{14}$$

where it is understood, that $\mu_n = N_e/(2\rho V)$ is an explicit function of N_e. The same applies to T_c, which is depens on N_e through μ_n and D as can be seen from Eq. 11. The logarithmic term $\ln(T/T_c)$ is a remnant of the logarithmic term in the expressions for the thermodynamic potential. As the series expansion in Δ is only valid near T_c we will replace it with $-(1 - T/T_c)$ in the remainder of this section.
The temperature dependance of the order parameter, as well as the behaviour of μ (using $\mu = \partial F/\partial N_e$) follow easily from the above Helmholtz free energy expression, and have exactly the same limiting behaviour near T_c as in the earlier expressions.

The entropy is calculated from Eq. 14 using $S = -(\partial F/\partial T)_{N_e,V,\Delta}$. (Alternatively one may use Eq. 9 with $S = -(\partial\Omega/\partial T)_{\mu,V,\Delta}$. The result is, of course, the same near the phase transition.)

$$S_s - S_n = \frac{-\rho V \Delta(T)^2}{T} \tag{15}$$

which is continuous at the critical temperature. From it we can now express the jump in the specific heat:

$$(c_n - c_s)\,|_{T=T_c} = -\frac{\rho V \beta^2 T_c}{1 + \frac{\beta^2 T_c^2}{8\mu_n^2}} \quad . \tag{16}$$

The term in the denominator as a reduction factor which is due to the coupling between the order parameter and μ.

The electronic pressure is obtained from the relation $p = -(\partial\Omega/\partial V)_{\mu,T}$ (using Eq. 9) while keeping μ and T fixed, where it is important that μ_n, T_c and D depend on volume. Near T_c the same result is obtained from differentiation of Eq. 14

$$\begin{aligned} p_s - p_n &= \rho\left[\mu^2 - \mu_n^2 + \tfrac{1}{2}\tfrac{\Delta^4}{\Delta^2+\beta^2T^2} + \tfrac{1}{2}\Delta^2\tfrac{d\ln D}{d\ln V}\right] \\ &= -B\rho\Delta(T)^2\tfrac{d\ln T_c}{dp} + O(\Delta^4) \quad , \end{aligned} \tag{17}$$

where in the last line we used Eq. 12.

So far we have left the elastic deformation energy of the crystal out of consideration. The bulk modulus relates changes in pressure to changes in volume: $\delta V = (B/V)\delta p$. This way we can now calculate the jump in expansivity ($\alpha \equiv d\ln V/dT$)

$$(\alpha_n - \alpha_s)\,|_{T=T_c} = -\frac{\rho\beta^2 T_c}{1 + \frac{\beta^2 T_c^2}{8\mu_n^2}} \frac{dT_c}{dp} \quad . \tag{18}$$

6. Discussion

The expansivity and specific heat jumps should obey the Ehrenfest relation [7]

$$\frac{dT_c}{dp} = V T_c \frac{\alpha_n - \alpha_s}{c_n - c_v} \tag{19}$$

which, comparing the expressions 16 and 18, is indeed satisfied. The corrections on the expansivity coefficient and the specific heat due to the coupling between the order parameter and the chemical potential are usually small: for the high T_c cuprates the ratio of T_c/T_F is about 6%, so that there is only a reduction of 0.1% of the specific heat jump. Vice versa, even if there is no direct coupling between the order parameter and the chemical potential, a jump in expansivity coefficient will contribute to the jump in $d\mu/dT$, because $\mu \propto V^{-1}$ in a layered 2D electron gas. The jump in expansivity of $YBa_2Cu_3O_7$ is about $-2 \cdot 10^{-7}K^{-1}$ [6], with a strong in-plane anisotropy and no contribution along the c-axis. The former could be related to the transfer of charge between planes and chains occuring at the onset of superconductivity as has been treated by Khomskii [8], the latter is consistent with the assumption of quasi-2D behaviour. As the effective Fermi temperature is about 1500 K we can estimate that due to the lattice anomaly there is a contribution to $(d\mu_s/dT - d\mu_n/dT)\,|_{T=T_c}$ of $3 \cdot 10^{-4}$. The observed effect is about 3 orders of magnitude larger [9], which implies that has a different origin. In particular the effect can be attributed to the coupling between ψ and μ assuming that T_c/T_F is about 0.06.

7. Conclusions

We generalized the Ginzburg-Landau free energy expression to incorporate the effect of the coupling of the order parameter to the chemical potential occurring in the BCS theory of a dilute interacting electron gas. We have shown that there is a jump in $d\mu/dT$ at the phase transition, and calculated the consequences of this effect for some of the other thermodynamic properties, in particular the specific heat and the expansivity parameter. The corrections do not change the nature of the transition, and they are small even in the range of parameters of high T_c cuprates with a relatively large T_c/T_F-ratio of about 0.06.

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[10] We have defined D as $4W\exp(-2/g)$. If the bandwidth is proportional to $V^{-\nu}$ we have $d\ln D/dp = (\nu/B) - (2/g)(d\ln g/d\ln p)$, where B is the bulkmodulus. Especially the pressure dependance of g can have any sign depending on the details of the mechanism for superconductivity.