Long range Coulomb forces and the behaviour of the chemical potential of electrons in metals at a second order phase transition.

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We give a general thermodynamic analysis of the behaviour of the chemical potential of electrons in metals at a second order phase transition, including in our analysis the effect of long range Coulomb forces. It is shown, that this chemical potential can have a kink at \(T_c\), both for fixed sample volume and fixed external pressure. The Coulomb term transfers the changes in chemical potential of the electrons into an experimentally observable shift of the surface potential if the sample is electrically connected to a ground potential.

I. INTRODUCTION

The behaviour of the chemical potential \((\mu^c)\) of electrons at the superconducting phase transition was discussed recently in Ref. [1–3], and corresponding measurements were carried out in Ref. [4]. It was shown theoretically, that in the BCS model \(\mu^c\) is given by the expression
\[
\mu^c = \mu^c_0 - \frac{\Delta^2}{\mu_0^2},
\]
or, if the density of states near \(E_F\) is energy dependent
\[
\mu^c = \mu^c_0(1 - \frac{d\rho}{dE} \Delta(T)^2),
\]
so that it has a kink at \(T_c\). General consideration gives for the kink the expression
\[
\frac{\Delta (d\mu^c/dT)_{\lambda\nu}}{\Delta C_V} = \frac{d\ln T_c}{dN_e}
\]
where \(N_e\) is the number of electrons and \(\Delta C_V\) is the jump in specific heat. This conclusion was confirmed experimentally [3], where it was shown that \(\mu^c\) in YBa\(_2\)Cu\(_3\)O\(_{7-x}\) does indeed have a kink at \(T_c\). This result is of an essentially thermodynamic nature and is actually independent of the specific nature of the phase transition, i.e. it is valid for other second order phase transitions as well, not only for superconductivity.

However, in Ref. [3] relation Eq. [3] was derived for a system at fixed volume, whereas the standard experiments are carried out at constant ambient pressure. For a system at constant pressure we should use the Landau expansion not for the Helmholtz free energy \(F(V,T,N,\psi)\), but the Gibbs free energy \(G(p,N,T,\psi)\), where \(\psi\) is an order parameter. Hence the well-known treatment [5] of phase transitions seems at first sight to rule out the possibility of obtaining a kink in \(\mu^c\): As the chemical potential is just this Gibbs free energy per particle, \(G = N\mu\), a kink in \(\mu\) is the hallmark of a first order phase transition [5], hence it seems paradoxal that a kink in the chemical potential was observed experimentally in a second order superconducting phase transition.

The situation, however, is not so simple, and the solution goes down to the definition of the chemical potential. The point is that, when dealing with metals, one usually discusses not the total chemical potential \(\mu\) determined as a Gibbs free energy per elementary cell or per mole of the substance, but the chemical potential of the electrons \(\mu^c\) (which at \(T = 0\) is equal to the Fermi energy). One may say that the total chemical potential \(\mu\) is the Gibbs free energy for adding to the system an extra unit cell, with all its nuclei and electrons, whereas \(\mu^c\) is the change in \(G\) when we change only the concentration of electrons. Thus, generally speaking, the situation here is similar to the situation in a mixtures, solutions or a complex chemical compound [5]. In that case we have to introduce chemical potentials for each component.
and whereas \( G \) itself, and the corresponding total chemical potential \( \mu = \partial G / \partial N = G / N \) (where \( N \) is the number of formula units for fixed concentration of components) should have no kink at \( T_c \) (this is actually the definition of a second order phase transition), partial chemical potentials \( \mu_i \) may well behave differently, as has been discussed for the high \( T_c \) ceramics by Burns \[7\]. The situation with \( \mu^c \) is still somewhat more complicated because, if we want to discuss it separately, i.e. if we want to look at the changes in the system when we change the electron concentration, we have also to take into account long range Coulomb forces, which usually guarantee electro-neutrality of the system. We will show below that, all these factors taken care of, the chemical potential of electrons \( \mu^e \) as measured e.g. in Ref \[4\] should indeed have a kink at \( T_c \), even if in the experiment not the volume but the pressure is fixed externally.

II. SINGLE COMPONENT SYSTEM.

First of all we derive Eq. \[1\] using a slightly different method than that used in \[3\], and show that indeed even for a one-component system the chemical potential at constant volume has a kink at the second order phase transition, in contrast to the situation at fixed pressure. At fixed pressure the Gibbs free energy \( G(p, T, N) = N \mu(p, T) \), and \( \mu(p, T) \) as well as the first derivatives of \( \mu \) are continuous at the transition. The temperature derivative of \( \mu \) at fixed pressure follows by making the transformation of variables \( \mu(V, T, N) = \mu(p(V, T), T) \), so that

\[
\left( \frac{d \mu}{dT} \right)_V = \left( \frac{d \mu}{dT} \right)_p + \left( \frac{d \mu}{dp} \right)_T \left( \frac{dp}{dT} \right)_V
\]

We furthermore identify \( (d \mu / dp)_T \) as \( V/N \). Only the second term of this expression gives rise to a discontinuity at the phase transition, for which we can use one of the Ehrenfest relations \[3\]

\[
\frac{\Delta (dp/dT)_V}{\Delta C_V} = \frac{d \ln T_c}{dN}
\]

As for a single component system \( NdT_c/dN = -VdT_c/dV \), we can now rewrite the Ehrenfest relation in the form

\[
\frac{\Delta (d \mu / dT)_V}{\Delta C_V} = \frac{d \ln T_c}{dN}
\]

which is identical to Eq. \[3\]. This treatment resolves the apparent contradiction between microscopic treatments, which give a finite jump in \( d \mu / dT \) at \( T_c \), and general arguments according to which \( \mu \) has to be smooth at a second order phase transition: As the microscopic treatments are carried out for a given electron concentration, and neglecting temperature dependencies of the volume, if the system is held at a constant external pressure. As we will show in the next section, the partial chemical potential of electrons may have a kink, even if such thermal changes of the volume are taken into account. Thus it is instructive to look for its behaviour first at fixed volume, such as is usually obtained from a microscopic description, and then make the Legendre transformation of the free energy \( G(p, N, T) = F(V, N, T) + pV \), to discuss the effects of fixing external pressure instead of volume. Important here is the role of the long range Coulomb interaction.

III. FIXED VOLUME

The thermodynamical state of the solid as follows from these conditions is described by the Helmholtz free energy \( F(V, T, N, N_e) \), where \( N \) is the number of elementary cells, and \( N_e \) is the number of electrons. Equivalently we can use the electron concentration \( x = N_e / N \), so that we can write the free energy in the form \( F(V, T, N, x) \). The Gibbs free energy per unit cell is \( \mu(V) = \left( \frac{dF}{dN} \right)_{V,T,x} \) and the chemical potential of the electrons is \( \mu^e(V) = N^{-1} \left( \frac{dF}{dN} \right)_{V,T,N} \). If the particles would be neutral, the free energy would depend on the volume as \( F = V f(n, x, T) \) where \( n = N/V \).

However if we want to discuss phenomena where the number of electrons is allowed to change, we should also add the Coulomb (charging) term, which has a different dependence on the size of the system. We use for the corresponding term the simple expression \( \delta F_C = e^2 N^2 (x - x_0)^2 / 2 \) (Coulomb energy of a charged sphere of radius \( R = V^{1/3} \) and charge \( eN(x - x_0) \) with \( x_0 \) the equilibrium number of electrons per unit cell). We will see later, that the precise shape of the sample, and therefore the exact value of the prefactor in \( \delta F_C \) is unimportant. Hence the Helmholtz free energy is
\begin{equation}
F(V, N, x, T) = V f(n, x, T) + \frac{1}{2} e^2 (x - x_0)^2 N^2 V^{-1/3}
\end{equation}

For systems where the external volume is fixed, the chemical potential of the electrons is

\begin{equation}
\mu^e(n, x, T, \phi) = \frac{1}{N} \frac{dE}{dn} \bigg|_{V, N, T} = \frac{1}{n} \frac{df}{dx} + e\phi
\end{equation}

where in the last line we introduced the charging potential \( \phi = e(x - x_0)n^{1/3}N^{2/3} \). If the sample is externally grounded, the electrons are in equilibrium with the ground potential which fixes \( \mu^e \) at the value of the external bath. The electrons can now flow freely in and out of the sample, so that the number of electrons follows from solving the above expression for \( x \). From this we see that the charge per unit cell \( x - x_0 \) is proportional to \( N^{-2/3} \). Note that the total chemical potential has a different form:

\begin{equation}
\mu(n, x, T) = \frac{dF}{dN} \bigg|_{V, x, T} = \frac{\delta T}{\delta n} + \phi^2 n^{-1/3} N^{-2/3}
\end{equation}

We see that, due to the fact that \( \phi \) is finite, the last (Coulomb) term vanishes in the thermodynamic limit. Clearly, as different partial derivatives are taken of the functional \( f(n, x, T) \), also a different behaviour at the phase transition occurs for \( \mu \) and \( \mu^e \). Both of them, however, would have a kink at \( T_c \): Using the continuity of entropy along the curve \( T_c(x) \) in the former, and \( T_c(n) \) in the latter case (as in Ref. [3]), one obtains Eq. 1 for the kink in \( d\mu^e/dT \), while

\begin{equation}
\Delta \left( \frac{d\mu}{dT} \right)_V = N^{-1} \Delta C_V \frac{d\ln T_c}{d\ln n}
\end{equation}

Hence the kink in \( d\mu/dT \) is proportional to the derivative of \( T_c \) with respect to the density of unit cells, which may also include a possible redistribution of electrons between reservoirs upon changing the lattice constant. On the other hand \( \Delta (d\mu^e/dT) \) is proportional to \( dT_c/dx \), where \( x \) is the number of electrons per unit cell. As was treated in Ref. [3], if the solid contains two charge reservoirs, one of which is active in the phase transition, a reduction of \( \Delta (d\mu^e/dT) \) occurs if a charge re-distribution between the reservoirs takes place at the phase transition. This also follows from the present thermodynamic analysis: \( dT_c/dx \) will be reduced, if part of the electrons moves into an inactive reservoir upon varying \( x \).

**IV. FIXED PRESSURE**

First of all we again obtain the general thermodynamic expression for the behaviour of \( \mu^e \) and \( (d\mu^e/dT)_p \) initially ignoring charging effects. Following [3] we differentiate the expression \( \Delta (\partial G/\partial T) = 0 \) (continuity of entropy) along the curve \( T_c(x) \) and find

\begin{equation}
0 = \frac{d}{dx} \Delta \left( \frac{\partial G}{\partial T} \right) = \left[ \frac{dT}{dx} \Delta \left( \frac{\partial^2 G}{\partial T^2} \right) + \Delta \left( \frac{\partial^2 G}{\partial T \partial x} \right) \right]_{T=T_c}
\end{equation}

so that

\begin{equation}
\Delta \left( \frac{d\mu^e}{dT} \right)_p = \frac{\Delta C_p}{N} \frac{d\ln T_c}{dx}
\end{equation}

Thus we see, that indeed if we could treat the electron concentration \( x \) as an independent parameter, the chemical potential of electrons \( \mu^e \) would have a kink at the second order phase transition, even at fixed pressure. Expression [11] has the same structure as Eq. 10, with the natural change of variables.

We can take into account charging effects, by going from \( F(V, N, x, T) \) to the Gibbs free energy \( G = F + pV \), where \( p = -\partial F/\partial V \), and calculate \( \mu^e(p, N, x, T) \equiv \partial G/\partial N_c \) and \( \mu(p, N, x, T) \equiv \partial G/\partial N_c \). As a result of the Legendre transformation, these have the same functional form as Eqs. 10 and 11. However, these expressions are in this case a function of \( p \), as the dependence of the density \( n \) on the external pressure has to be solved from

\begin{equation}
p(n, x, T) = -f(n, x, T) + n \frac{\delta f}{\delta n} + \frac{1}{6} \phi^2 n^{2/3} N^{-2/3}
\end{equation}

As before \( \phi \), defined as \( e(x - x_0)n^{1/3}N^{2/3} \), is the charging potential. Note that the Coulomb term introduces an additional dependence on the total number of unit cells \( N \), due to its long range nature. Hence in principle we should consider \( n(p, T, x, N) \). However, this contribution vanishes for \( N \to \infty \).
\[
\mu_\varepsilon(p, x, T, \phi) = \frac{1}{2} \frac{\partial F}{\partial p} + e\phi \\
\mu(p, x, T) = \frac{\partial f}{\partial n} + \phi^2 n^{-1/3} N^{-2/3}
\] (13)

As \( \mu \) has to be evaluated at the minimum with respect to the order parameter, it is automatically ensured that it has no kink at the phase transition, provided that a Landau expansion can be made. We also notice, that the charging effects do not affect our expression for the kink in \( \mu^\varepsilon \) (Eq. 11), as the charging term is of vanishing order for \( N \to \infty \): If the sample is electrically isolated \( N \) and \( x \) are fixed. As \( \phi = e(x - x_0)n^{1/3}N^{2/3} \), the only thermal variations enter through the volume changes (changes of \( n \)). Hence, if the sample is electrically charged, there are temperature dependent changes to \( \mu_\varepsilon \) due to changes in lattice constant at fixed external pressure, that should be taken into account. If, on the other hand the sample is electrically grounded, \( \mu_\varepsilon \) is fixed externally. In this case \( e\phi \) is exactly equal to \( \mu_\varepsilon \) (but with opposite sign) of the electrically isolated uncharged sample, and can be measured experimentally.

V. EXAMPLE

For a solid undergoing a second order phase transition, we may write \( f(n, x, T, \psi) = f_0 + f_\psi \), where for \( f_0 \) and \( f_\psi \) we make the following free energy expansion

\[
F_0(N, V, T, \psi) = (\mu_0 + \mu_\psi)N + \frac{1}{2} B_0 V_0 \left( \frac{V - V_0}{V_0} - 1 \right) + c(V - V_0) |\psi|^2 + \frac{1}{2} \phi^2 V^{1/3}
\]

\[
\mu_\psi(n, T, \psi) = a(T - T_c)|\psi|^2 + \frac{b}{2} |\psi|^4 + \frac{c}{3} n^{1/3} N^{-2/3}
\] (14)

It has to be understood here, that the parameters \( a, b, \) and \( T_c \) are independent of the volume \( V \), and coupling between the strain field and the superconducting order parameter is introduced in an ad-hoc manner through the constant \( c \). The expression for the pressure as occurs in Eq. (12) is

\[
p = -B_0 \left[ \frac{V}{V_0} - 1 \right] - c|\psi|^2 + \frac{1}{6} \phi^2 V^{-2/3}
\] (15)

from which we solve the volume \( V = V_0 \left\{ 1 - (p + c|\psi|^2)/B_0 \right\} \). We are now ready to calculate the Gibbs free energy, and from it, with the definition of \( \mu \), the chemical potential

\[
\mu(p, T, \psi) = \mu_0 + \frac{p}{n_0} \left[ 1 - \frac{p}{2B_0} \right] + \left[ a(T - T_c) - \frac{c}{n_0 B_0} \right] |\psi|^2 + \frac{1}{2} \left[ b - \frac{c^2}{n_0 B_0} \right] |\psi|^4 + \frac{2}{3} \phi^2 N^{-1/3} N^{-2/3}
\] (16)

Here \( n_0 \equiv N/V_0 \) represents the molar density of the solid if the order parameter is zero. So in the first place we notice, that in spite of the coupling to the lattice, the transition remains of second order. Only if the coupling constant \( c \) exceeds the critical value \( (b n_0 B_0)^{1/2} \), it becomes of first order. In the second place we notice that, in the case where the transition is still of second order, \( T_c \) is shifted with an amount and direction which depends on \( c \) and the value of the externally applied pressure. The Gibbs free energy per particle calculated at the minimum with respect to \( |\psi|^2 \) is

\[
\mu(p, T) = \mu_0 + \frac{p}{n_0} \left[ 1 - \frac{p}{2B_0} \right] - \frac{a^2(T - T_c)^2}{2b} + \frac{2}{3} n^{-1/3} N^{-2/3}
\]

\[
T_c(p) = T_c + \frac{p}{n_0 B_0} \left\{ 1 - \frac{p}{2B_0} \right\}
\]

\[
\frac{c}{n_0 B_0}
\] (17)

Clearly the total chemical potential of the system has a smooth behaviour at the phase transition without a kink, unless the coupling to the lattice is sufficiently strong to make the transition first order.

Let us now consider the electronic sub-system. As we are considering a solid, the number of unit cells, \( N \), is externally fixed, and the corresponding chemical potential need not be in equilibrium with an external bath. The situation is completely different for the electrons however, as these can move in and out of the solid. Using again the definition \( x = N_c/N \) for the number of electrons per unit cell, we can calculate the corresponding chemical potential by differentiating the total Gibbs free energy (\( \mu_N \), where \( \mu \) is the chemical potential as calculated above) with respect to \( N_c \). As we have seen in the preceding section, the long range Coulomb forces can be included, and the correct expression becomes \( \mu_\varepsilon(p) = \frac{\partial \mu}{\partial x} \mid_{p,T} + e\phi \), where we have to assume now that \( \mu \) not only depends on \( p \) and \( T \), but also on \( x \). Indeed most of the properties of a solid depend strongly on the number of charge carriers per unit cell, for example by influencing the strength of the chemical bond between neighbouring unit cells, or by having an effect on
the superconducting transition temperature. For our discussion the latter dependence is the most important one, as we are interested in the behaviour near the superconducting transition. Let us indeed assume that \( \mu_e \) is derived from a microscopic theory, which also predicts that \( dT_c / dx \neq 0 \). If the electronic subsystem is brought into equilibrium with an external bath by connecting it with a current lead, the charge on the sample is such, that \( e\phi \) compensates for the difference. Hence \( \mu^e (p) = \mu^{ext} \) and the voltage on the sample is

\[
e\phi = \mu^{ext} - \mu_n - \frac{a^2(T - \tilde{T}_c)}{b} \frac{dT_c}{dx} \tag{18}
\]

This voltage has a kink at \( \tilde{T}_c \), which can be determined experimentally by measuring the work function of the sample. If the lattice is sufficiently soft (\( B_0 \leq c^2/n_0b \)) the transition becomes of first order. The above expression diverges at the point where \( B_0 = c^2/n_0b \) and is no longer valid in this limit. If the material is hard (\( B_0 \gg c^2/n_0b \)) and the external pressure small (\( p \ll n_0aB_0/c \)) Eq. (18) is just the result which we already obtained at fixed sample volume.

VI. CONCLUSIONS

The seemingly paradoxal result of microscopic theories of superconductivity, that the chemical potential may have a kink at a \textit{second order} phase transition, is resolved. There are two ingredients in the resolution of the paradox. The first is, that the microscopic treatment is always carried out at a given concentration of electrons, \textit{i.e.} at fixed volume or density. In contrast to fixed pressure, there is absolutely no general rule forbidding the kink in \( \mu \) at fixed volume; general thermodynamic results [3] confirm that. More interesting is the second part of the story. The chemical potential of the electrons is in general different from the total chemical potential and thus can have a kink, even at fixed pressure. This stems from the fact that electrons are free to move in and out of a solid, thus maintaining electrical equilibrium with the environment, whereas the ions in a solid are immobile. As a result the chemical potential of electrons and the Gibbs free energy per mole of the ions have different dependencies on temperature, pressure etc., and are only coupled through the long range Coulomb forces. Using scaling arguments the Coulomb charging energy is shown to be of vanishing order in the Gibbs free energy per unit cell, the density of the solid, \( T_c \) and the order parameter. At the same time the long range Coulomb forces on the one hand keep the charge carrier density fixed, while on the other hand they transform changes of the chemical potential of the electrons into equally large and measurable changes of the work function, if the solid is in electrical equilibrium with its environment.

VII. ACKNOWLEDGEMENTS

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