

Long-range Coulomb forces and the behavior 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 behavior 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 behavior of the chemical potential (μ^e) of electrons at the superconducting phase transition was discussed recently in Refs. 1–3, and corresponding measurements were carried out in Ref. 4. It was shown theoretically that in the BCS model μ^e is given by the expression $\mu^e = \mu_0^e - \frac{\Delta^2}{4\mu_0}$, or, if the density of states near E_F is energy dependent $\mu^e = \mu_0^e [1 - \frac{d\rho/dE}{\rho} \Delta(T)^2]$, so that it has a kink at T_c . General consideration gives for the kink the expression

$$\frac{\Delta (d\mu^e/dT)_V}{\Delta C_V} = \frac{d \ln T_c}{dN_e}, \quad (1)$$

where N_e is the number of electrons and ΔC_V is the jump in specific heat. This conclusion was confirmed experimentally,⁴ where it was shown that μ^e in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ 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 (1) 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 ψ is an order parameter. Hence the well-known treatment⁵ of phase transitions seems at first sight to rule out the possibility of obtaining a kink in μ : As the chemical potential is just this Gibbs free energy per particle, $G = N\mu$, a kink in μ is the hallmark of a first-order phase transition,⁵ hence it seems paradoxical that a kink in the chemical potential was observed experimentally in a second-order supercon-

ducting 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 μ determined as a Gibbs free energy per elementary cell or per mole of the substance, but the chemical potential of the electrons μ^e (which at $T = 0$ is equal to the Fermi energy). One may say that the total chemical potential μ is the Gibbs free energy for adding to the system an extra unit cell, with all its nuclei and electrons, whereas μ^e 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 mixtures, solutions or a complex chemical compound.⁵ In that case we have to introduce chemical potentials for each component

$$G = \sum_i \mu_i N_i \quad (2)$$

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 μ_i may well behave differently, as has been discussed for the high- T_c ceramics by Burns.⁷ The situation with μ^e 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 also have to take into account long-range Coulomb forces, which usually guarantee electroneutrality of the system. We will show below that all these factors taken care of, the chemical potential of electrons μ^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 Ref. 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 μ are continuous at the transition. The temperature derivative of μ at fixed pressure follows by making the transformation of variables $\mu(V, T) = \mu[p(V, T), T]$, so that

$$\left(\frac{d\mu}{dT}\right)_V = \left(\frac{d\mu}{dT}\right)_p + \left(\frac{d\mu}{dp}\right)_T \left(\frac{dp}{dT}\right)_V. \quad (3)$$

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 relations⁵

$$\frac{\Delta(dp/dT)_V}{\Delta C_V} = -\frac{d \ln T_c}{dV}. \quad (4)$$

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

$$\frac{\Delta(d\mu/dT)_V}{\Delta C_V} = \frac{d \ln T_c}{dN} \quad (5)$$

which is identical to Eq. (1). 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 μ has to be smooth at a second-order phase transition: As mentioned in the Introduction the microscopic treatment is carried out for a given electron concentration⁵ at fixed volume, whereas the thermodynamic treatment forbids the kink in $\mu(T)$ in a one-component system at a constant external pressure. We will show in the next section, that the partial chemical potential of electrons may have a kink, even at fixed pressure, if the thermal changes of the volume are taken into account. Thus it is instructive to look for its behavior 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 $\mu(V) = \left(\frac{\partial F}{\partial N}\right)_{V, T, x}$ and the chemical potential of the elec-

trons is $\mu^e(V) = N^{-1} \left(\frac{\partial F}{\partial x}\right)_{V, T, N}$. If the particles would be neutral, the free energy would depend on the volume as $F = Vf(n, x, T)$ 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 $\delta F_C = \frac{e^2 N^2 (x - x_0)^2}{2V^{1/3}}$ [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, Thomas-Fermi screening has no effect on the macroscopic charging energy of the sample]. We will see later that the precise shape of the sample, and therefore the exact value of the prefactor in δF_C , is unimportant. Hence the Helmholtz free energy is

$$F(V, N, x, T) = Vf(n, x, T) + \frac{1}{2}e^2(x - x_0)^2 N^2 V^{-1/3}. \quad (6)$$

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

$$\mu^e(n, x, T, \phi) = \frac{1}{N} \frac{dF}{dx} \Big|_{V, N, T} = \frac{1}{n} \frac{\partial f}{\partial x} + e\phi, \quad (7)$$

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 μ^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:

$$\mu(n, x, T) = \frac{dF}{dN} \Big|_{V, x, T} = \frac{\partial f}{\partial n} + \phi^2 n^{-1/3} N^{-2/3}. \quad (8)$$

We see that, due to the fact that ϕ 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 behavior at the phase transition occurs for μ and μ^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

$$\Delta \left(\frac{d\mu}{dT}\right)_V = N^{-1} \Delta C_V \frac{d \ln T_c}{d \ln n}. \quad (9)$$

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 the dT_c/dx , where x is the number of electrons per unit cell. As was treated in Ref. 2, 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 redistribution 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 behavior of μ^e and $(d\mu^e/dT)_p$ initially ignoring charging effects. Following Ref. 6 we differentiate the expression $\Delta(\partial G/\partial T) = 0$ (continuity of entropy) along the curve $T_c(x)$ and find

$$0 = \frac{d}{dx} \Delta \left(\frac{\partial G}{\partial T} \right) = \left[\frac{dT}{dx} \Delta \left(\frac{\partial^2 G}{\partial T^2} \right) + \Delta \left(\frac{\partial^2 G}{\partial T \partial x} \right) \right]_{T=T_c} \quad (10)$$

so that

$$\Delta \left(\frac{d\mu^e}{dT} \right)_p = \frac{\Delta C_p}{N} \frac{d \ln T_c}{dx} \quad (11)$$

Thus we see that, indeed if we could treat the electron concentration x as an independent parameter, the chemical potential of electrons μ^e would have a kink at the second-order phase transition, even at fixed pressure. Expression (11) has the same structure as Eq. (1), 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 $\mu^e(p, N, x, T) \equiv \partial G/\partial N_e$ and $\mu(p, N, x, T) \equiv \partial G/\partial N$. As a result of the Legendre transformation, these have the same functional form as Eqs. (7) and (8). 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

$$p(n, x, T) = -f(n, x, T) + n \frac{\partial f}{\partial n} + \frac{1}{6} \phi^2 n^{2/3} N^{-2/3} \quad (12)$$

As before ϕ , 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 $N \rightarrow \infty$:

$$\begin{aligned} \mu^e(p, x, T, \phi) &= \frac{1}{n} \frac{\partial f}{\partial x} + e\phi, \\ \mu(p, x, T) &= \frac{\partial f}{\partial n} + \phi^2 n^{-1/3} N^{-2/3}. \end{aligned} \quad (13)$$

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

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 $(bn_0 B_0)^{1/2}$, it becomes of first order. In the second place we notice that,

As μ 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 μ^e [Eq. (11)], as the charging term is of vanishing order for $N \rightarrow \infty$: 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 μ^e 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, μ^e is fixed externally. In this case $e\phi$ is exactly equal to μ^e (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_ψ we make the following free energy expansion:

$$\begin{aligned} F_0(N, V, T, \psi) &= (\mu_0 + \mu_\psi)N + \frac{1}{2} B_0 V_0 \left(\frac{V}{V_0} - 1 \right)^2 \\ &\quad + c(V - V_0) |\psi|^2 + \frac{1}{2} \phi^2 V^{1/3}, \\ \mu_\psi(n, T, \psi) &= a(T - T_c) |\psi|^2 + \frac{b}{2} |\psi|^4. \end{aligned} \quad (14)$$

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 .⁸ The expression for the pressure as occurs in Eq. (12) is

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

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

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 ψ^2 is

$$\begin{aligned} \mu(p, T) &= \mu_0 + \frac{p}{n_0} \left[1 - \frac{p}{2B_0} \right] - \frac{a^2(T - \tilde{T}_c)^2}{2\tilde{b}} \\ &\quad + \frac{2}{3}n^{-1/3}N^{-2/3}, \\ \tilde{T}_c(p) &= T_c + p \frac{c}{n_0 B_0 a}, \\ \tilde{b} &= b - \frac{c^2}{n_0 B_0}. \end{aligned} \quad (17)$$

Clearly the total chemical potential of the system has a smooth behavior 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 subsystem. 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 $x = N_e/N$ for the number of electrons per unit cell, we can calculate the corresponding chemical potential by differentiating the total Gibbs free energy (μN , where μ is the chemical potential as calculated above) with respect to N_e . As we have seen in the preceding section, the long-range Coulomb forces can be included, and the correct expression becomes $\mu^e(p) = \left. \frac{\partial \mu}{\partial x} \right|_{p, T} + e\phi$, where we have to assume now that μ 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 neighboring 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 behavior near the superconducting transition. Let us indeed assume that μ_ψ 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 $\mu^e(p) = \mu^{\text{ext}}$ and the voltage on the sample is

$$e\phi = \mu^{\text{ext}} - \mu_n - \frac{a^2(T - \tilde{T}_c)}{\tilde{b}} \frac{d\tilde{T}_c}{dx}. \quad (18)$$

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 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 paradoxical result of microscopic theories of superconductivity, that the chemical potential may have a kink at a *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, i.e., at fixed volume or density. In contrast to fixed pressure, there is absolutely no general rule forbidding the kink in μ at fixed volume; general thermodynamic results³ 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.

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