# BCS Theory and Superconductivity

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## 1. Introduction

Superconductivity discovered in 1911 by Onnes (9), is the quantum phenomena that certain materials exhibit under particular magnetic and temperature regimes. There existed no consistent microscopic theory that described why superconductivity arose, from the time it was discovered until the 1950's, only macroscopic theories that allowed you to calculate certain thermodynamic and electrodynamic quantities. In 1957, two papers released by Bardeen, Cooper, and Schrieffer (1) (2) described the conceptual and mathematical foundation for conventional superconductivity, the Bardeen-Cooper-Schrieffer (BCS) theory, for which they later received the Nobel Prize for in 1972.

We will look at features of superconductors before the discovery of the BCS theory, and examine the assumptions and methods used to develop the theory. We will then calculate and study interesting quantities of the superconducting system, and finally describe how the results predicted by the BCS theory fare against experimental evidence obtained about superconductors.

## 2. Before BCS Theory

### 2.1 Aspects of Superconductivity

Onness discovery of superconductivity came when he witnessed a sudden drop in the resistance of solid mercury at 4.2 K. All superconductors show this drop of resistance, either gradually or suddenly, at a particular transition temperature, $T_c$. Infinite conductivity implies that if a current were passed through the material during its superconducting phase, the current would follow forever without any dissipation.

Another characteristic, later found by Meissner and Ochsenfeld (8), is that all superconductors are diamagnets. Diamagnetism occurs when an external magnetic field penetrates only a finite, amount of the material, and does not hinder the remaining inner parts of the material. The penetration depth is usually small compared to the width of the material. Also known as the Meissner effect, this event also indicates that a particular magnetic field would destroy the superconductivity of a material.

The isotope effect discovered by Maxwell and Reynolds describes the relation between $T_c$ and the isotopic mass of the superconductor (7) (11). This information based on experiments on naturally occurring mercury and its isotope, observed a decrease in $T_c$ with an increase in isotopic mass. This allows for the assumption that the basis of superconductivity relies on electron-phonon interactions, an assumption that would later lead to the formation of the BCS theory.

### 2.2 In search of a microscopic theory

Because superconductivity was found in materials before the physics community predicted the phenomena, theories were formed to attempt to explain, match and predict the characteristics of these materials that undergo the phase transition. London and London were interested in superconductivity but did not attempt to describe the reason for it. Instead, they derived an equation for the penetration depth, $\lambda$, of the superconductor (4), but their results consistently overestimated the experimentally found values, and so their assumptions were discarded.

The Ginzburg-Landau theory in 1950 (6), was a phenomenological theory using physical intuition and the variational principle of quantum mechanics. It allowed the calculation of macroscopic quantities of the material in the superconducting state if one assumed the phase transition to be of second order. His results were able to accurately match the experimental results of the time, and were later shown to be a specific form of the BCS theory. While useful and accurate for macroscopic quantities, like the London-London attempt, it did not explain the foundation for superconductivity in these materials.

## 3. Foundations of BCS Theory

In this section, we lay out the theoretical grounds for BCS theory. All derivations may be referenced in "Theory of Superconductivity" by Bardeen, Cooper, and Schrieffer or Tinkham's *Introduction to Superconductivity*.

### 3.1 Cooper Pairs

The BCS theory relies on the assumption that superconductivity arises when the attractive Cooper pair interaction dominates over the repulsive Coulomb force (2). A Cooper pair is a weak electron-electron bound pair medi-

ated by a phonon interaction. Although somewhat ambiguous, one can visualize this pairing by the following explanation. Imagine an electron moving within a material. The Coulomb attraction between the electron and the positively charged cores of ions in the material will leave a net positive charge in the vicinity. A "paired" electron is one with opposite momentum and spin that is attracted to this force.

This heuristic explanation is somewhat incomplete, because at the heart of the phonon-mediated interaction is a long range attraction and thus, requires quantum mechanics for a full explanation. Cooper's monumental 1956 work showed that due to the fermi statistics of the electron, this paired $e^- - e^-$ state can have energy less than that of the Fermi-energy of the material(3). Thus, at adequately low temperatures, when thermal energy is not a factor, bound $e^- - e^-$ states can form.

We give a short, simplified argument of for this fact. Suppose we have two electrons interacting with this attractive Cooper force with a background Fermi sea at $T = 0$ by which these electrons only interact via Pauli-exclusion. We look for a zero-momentum wave-function of the form:

$$\Psi(\mathbf{r}_0, \mathbf{r}_1) = \sum_{\mathbf{k}} g_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r_2})} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right).$$

Antisymmetry demands $g_{\mathbf{k}} = g_{-\mathbf{k}}$. Placing this in the Schrödinger equation $H\Psi = E\Psi$ yields the following condition:

$$(E - 2\epsilon_{\mathbf{k}}) g_{\mathbf{k}} = \sum_{\mathbf{k}' > \mathbf{k}_F} V_{\mathbf{k}\mathbf{k}'} g_{\mathbf{k}'}$$

where $V_{\mathbf{k}\mathbf{k}'} = \frac{1}{\text{vol}} \int_{\text{vol}} d^3r \; V(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}$. Now the following mean field approximation is made:

$$V_{\mathbf{k}\mathbf{k}'} = \begin{cases} -V & \text{for } \epsilon_F < \epsilon_{\mathbf{k}} < \epsilon_F + \hbar\omega_c \\ 0 & \text{else} \end{cases}$$

where $\epsilon_F$ is the Fermi energy and $\omega_c$ is a cutoff frequency. This indicates that we only consider interactions that are allowed by the metal's frequency range, similar to the assumptions made in the Debeye model. We then have

$$\begin{aligned} \frac{1}{V} &= \sum_{\mathbf{k} > \mathbf{k}_F} \frac{1}{2\epsilon_{\mathbf{k}} - E} \\ &\to N_0 \int_{\epsilon_F}^{\epsilon_F + \hbar\omega_c} \frac{d\epsilon}{2\epsilon - E} \\ &= \frac{N_0}{2} \ln\left(\frac{2\epsilon_F - E + 2\hbar\omega_c}{2\epsilon_F - E}\right) \end{aligned}$$

Simplifying:

$$\frac{1}{2\hbar\omega_c}(2\epsilon_F - E) = \frac{1}{e^{2/N_0 V} - 1} \approx e^{-2/N_0 V}$$

for $N_0 V \ll 1$. Thus, the energy of the pair satisfies

$$E = 2\epsilon_F - 2\hbar\omega_c e^{-2/N_0 V} < 2\epsilon_F. \tag{1}$$

### 3.2 The model

We now proceed to write down the model Hamiltonian for the theory. This is most easily done in the language of second quantization. Let $c_{\mathbf{k}\sigma}$ and $c^\dagger_{\mathbf{k}\sigma}$ to be electron annihilation and creation operators of momentum $\mathbf{k}$ and spin $\sigma = \uparrow$ or $\downarrow$. The usual commutation relations are:

$$\{c_{\mathbf{k}\sigma}, c^\dagger_{\mathbf{k}'\sigma}\} = \delta^{(3)}(\mathbf{k} - \mathbf{k}')\delta_{\sigma\sigma'}$$

and

$$\{c_{\mathbf{k}\sigma}, c_{\mathbf{k}'\sigma}\} = 0 = \{c^\dagger_{\mathbf{k}\sigma}, c^\dagger_{\mathbf{k}'\sigma}\}.$$

The proposed Hamiltonian is taken to be

$$H' = \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\mathbf{l}} V_{\mathbf{k}\mathbf{l}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow} c_{-\mathbf{l}\downarrow} c_{\mathbf{l}\uparrow}. \tag{2}$$

The first term is the usual kinetic energy of the electrons. The second term is the translation of the phonon mediated electron-electron interaction into this framework. The matrix element $V_{\mathbf{k}\mathbf{k}'}$ may be taken to be general, but we shall simplify it by using the mean field approximation mentioned earlier in later calculations.

Now, in a normal state we would expect no formation of Cooper pairs, hence the operator $c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow}$ should average out to zero. It is then natural to define the quantity

$$b_{\mathbf{k}} = \langle c_{\mathbf{k}\uparrow} c_{-\mathbf{k}\downarrow} \rangle.$$

The so-called gap energy is then defined to be

$$\Delta_{\mathbf{k}} = -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} b_{\mathbf{k}'}. \tag{3}$$

To allow the exchange of particles it makes sense to consider the new Hamiltonian $H = H' + \mu N$ where $\mu$ is the chemical potential.

The Hamiltonian can be diagonalized following the method of Bogoliubov. We defined the linearly transformed states $\gamma_{\mathbf{k}0}$ and $\gamma_{\mathbf{k}1}$ by

$$\begin{aligned} c_{\mathbf{k}\uparrow} &= u^*_{\mathbf{k}} \gamma_{\mathbf{k}0} + v_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}1} \\ c^\dagger_{\mathbf{k}\downarrow} &= -v^*_{\mathbf{k}} \gamma_{\mathbf{k}0} + u_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}1} \end{aligned}$$

such that $|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$. In practice, we can let one of $u_{\mathbf{k}}$ or $v_{\mathbf{k}}$ be real. To complete the diagonaization we look at the the Hamiltonian in this basis:

$$\begin{aligned} H' = \sum_k \Big\{ & \xi_{\mathbf{k}} \Big( (|u_{\mathbf{k}}|^2 - |v_{\mathbf{k}}|^2)(\gamma^\dagger_{\mathbf{k}1}\gamma_{\mathbf{k}1} + \gamma^\dagger_{-\mathbf{k}0}\gamma_{-\mathbf{k}0}) \\ & + 2|v_{\mathbf{k}}|^2 + 2u^*_{\mathbf{k}} v^*_{\mathbf{k}} \gamma_{-\mathbf{k}0}\gamma_{\mathbf{k}1} + 2u_{\mathbf{k}} v_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}1}\gamma^\dagger_{-\mathbf{k}0} \Big) \\ & \Big( (\Delta_{\mathbf{k}} u_{\mathbf{k}} v^*_{\mathbf{k}} + \Delta^*_{\mathbf{k}} u^*_{\mathbf{k}} v^*_{\mathbf{k}})(\gamma^\dagger_{\mathbf{k}1}\gamma_{\mathbf{k}1} + \gamma^\dagger_{-\mathbf{k}0}\gamma_{-\mathbf{k}0} - 1) \\ & + (\Delta_{\mathbf{k}} (v_{\mathbf{k}})^* - \Delta^*_{\mathbf{k}} (u_{\mathbf{k}})^*)\gamma_{-\mathbf{k}0}\gamma_{\mathbf{k}1} \\ & + (\Delta^*_{\mathbf{k}} v^2_{\mathbf{k}} - \Delta_{\mathbf{k}} u^2_k)\gamma^\dagger_{\mathbf{k}1}\gamma^\dagger_{-\mathbf{k}0} + \Delta_{\mathbf{k}} b^*_{\mathbf{k}}) \Big\}. \end{aligned}$$

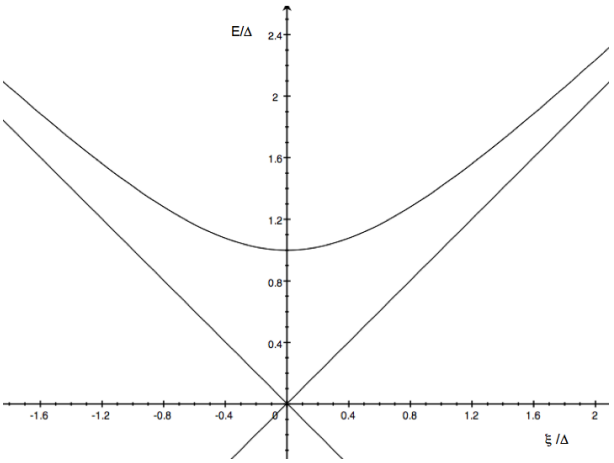



Figure 1: The energy gap seen between the superconducting state (top) and the normal state (bottom) produces the order parameter of the system.

We determine the $u$ and $v$ terms by demanding the coefficients of $\gamma_{-\mathbf{k}0}\gamma_{\mathbf{k}1}$ and $\gamma^\dagger_{\mathbf{k}1}\gamma^\dagger_{-\mathbf{k}0}$. This is equivalent to

$$\frac{\Delta^*_{\mathbf{k}} v_{\mathbf{k}}}{u_k} = \sqrt{\xi^2_{\mathbf{k}} + |\Delta_{\mathbf{k}}|^2} - \xi_{\mathbf{k}} \equiv E_{\mathbf{k}} - \xi_{\mathbf{k}}$$

where

$$E_{\mathbf{k}} \equiv \sqrt{\xi^2_{\mathbf{k}} + |\Delta_{\mathbf{k}}|^2}.$$

From this we observe that the gap energy $\Delta_{\mathbf{k}}$ is the order parameter for this interacting theory as seen in Fig. 1.

The graph also indicates with the order parameter that the superconducting state still has energy greater than zero with no kinetic energy, unlike the normal state. The role of this order parameter will become even more apparent with further calculations of thermodynamic quantities.

Our objective now is to find a BCS ground state. That is, one that the transformed Bogoliubov operators act on. If $|0\rangle$ is the free ground state, the most general candidate for the BCS ground state would be a wave function of the form

$$|\Psi_0\rangle \sim \prod_{\mathbf{k},\sigma} \gamma_{\mathbf{k}\sigma} |0\rangle$$

as this state is killed by $\gamma_{\mathbf{k}\sigma}$ for any $\sigma$ because $\gamma_{\mathbf{k}\sigma}\gamma_{\mathbf{k}\sigma} \equiv 0$. By substituting our original electron operators, this says that the BCS ground state has the form

$$|\mathrm{BCS}\rangle = \prod_{\mathbf{k}} \left(u_{\mathbf{k}} + v_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} c^\dagger_{-\mathbf{k}\downarrow}\right) |0\rangle . \tag{4}$$

Once we have this ground state, we may obtain superconducting excited states by

$$\gamma^\dagger_{\mathbf{k}_1\sigma_1}\gamma^\dagger_{\mathbf{k}_2\sigma_2}\cdots\gamma^\dagger_{\mathbf{k}_n\sigma_n} |\mathrm{BCS}\rangle .$$

This is analogous to the raising and lowering operators acting on the ground state of the one-dimensional simple harmonic oscillator.

## 4. Thermodynamic Calculations

### 4.1 Evaluating $T_c$

By definition of $\Delta_{\mathbf{k}}$ and $\gamma_{\mathbf{k}\sigma}$, we have

$$\begin{aligned}\Delta_{\mathbf{k}} &= -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} b_{\mathbf{k}'} \\ &= -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u^*_{\mathbf{k}} v_{\mathbf{k}'} \left\langle 1 - \gamma^\dagger_{\mathbf{k}'0}\gamma_{\mathbf{k}'0} - \gamma^\dagger_{\mathbf{k}'1}\gamma_{\mathbf{k}'1}\right\rangle .\end{aligned}$$

Now, $\gamma^\dagger_{\mathbf{k}0}\gamma_{\mathbf{k}0} = \delta(\mathbf{k}-\mathbf{k}') = \gamma^\dagger_{\mathbf{k}'1}\gamma_{\mathbf{k}'1}$ thus,

$$\begin{aligned}\Delta_{\mathbf{k}} &= -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u^*_{\mathbf{k}} v_{\mathbf{k}'} \left\langle 1 - \gamma^\dagger_{\mathbf{k}'0}\gamma_{\mathbf{k}'0} - \gamma^\dagger_{\mathbf{k}'1}\gamma_{\mathbf{k}'1}\right\rangle \\ &= -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u^*_{\mathbf{k}'} v_{\mathbf{k}'} \left(1 - 2(f(E_{\mathbf{k}'})\right) \\ &= -\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{2E_{\mathbf{k}'}} \tanh\left(\frac{\beta E_{\mathbf{k}}}{2}\right) \\ &= \frac{V}{2}\sum_{\mathbf{k}'} \frac{\Delta_{\mathbf{k}'}}{E_{\mathbf{k}'}} \tanh\left(\frac{\beta E_{\mathbf{k}}}{2}\right).\end{aligned}$$

In the last step, we have made the usual mean field approximation $V_{\mathbf{k}\mathbf{k}'} = -V$. In this approximation we know then that $\Delta_{\mathbf{k}}$ is independent of $\mathbf{k}$. Thus, we have the relation

$$\frac{1}{V} = \frac{1}{2}\sum_{\mathbf{k}'} \frac{\tanh\left(\frac{\beta E_{\mathbf{k}}}{2}\right)}{E_{\mathbf{k}'}} \tanh\left(\frac{\beta E_{\mathbf{k}}}{2}\right)$$

We know that generally $E_{\mathbf{k}} = \sqrt{\xi^2_{\mathbf{k}} + \Delta^2}$, and at the transition temperature the energy gap, $\Delta$, vanishes leaving the relation: $E_{\mathbf{k}} = |\xi_{\mathbf{k}}|$, which is symmetric about the Fermi energy. Then,

$$\begin{aligned}\frac{1}{V} &= 2\cdot\frac{1}{2}\sum_{\mathbf{k}'} \frac{\tanh\left(\frac{\beta\xi_{\mathbf{k}}}{2}\right)}{\xi_{\mathbf{k}'}} \tanh\left(\frac{\beta\xi_{\mathbf{k}}}{2}\right) \\ &\to N_0 \int_0^{\epsilon_c} d\xi \frac{1}{\xi} \tanh\left(\frac{\beta\xi}{2}\right).\end{aligned}$$

We will evaluate the integral from $\xi = 0$ to the Cooper energy, $\epsilon_c = \hbar\omega_c$, where the transition to superconductivity begins. Note that we expect $\omega_c \simeq \omega_D$ the Debye frequency. This is due to the dependence of the Cooper formation having phonons exist within the material.

To compute this integral, we make the substitution $x = \frac{\beta\xi}{2}$ to get,

$$\frac{1}{N_0 V} = \int_0^{\beta_c\epsilon_c/2} \frac{\tanh(x)}{x} dx.$$

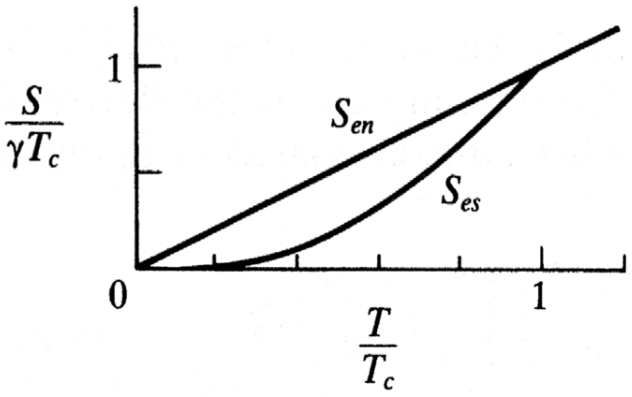



Figure 2: Comparing the entropy dependence on temperature (12), we see that the superconducting state, $S_{es}$, is more ordered than the normal state $S_{en}$.

We can evaluate this integral approximately,

$$\frac{1}{N_0 V} \approx \ln(1.13\ \beta_c \hbar\omega_c)$$

which gives

$$k_B T_c \approx 1.13\ \hbar\omega_c e^{-1/N_0 V}. \tag{5}$$

### 4.2 Entropy

A thermodynamic quantity that may be calculated is the entropy of the system in different phases. We have previously derived that for a Fermi gas, in this case the free electrons of the material, the entropy $S_{en}$ is proportional to $T$. For the superconducting state with Fermi function

$$f_{\mathbf{k}} := f(E_{\mathbf{k}}) = \frac{1}{1 + e^{\beta E_{\mathbf{k}}}}$$

the entropy is given by

$$S_{\text{es}} = -2k_B \sum_{\mathbf{k}} \{(1 - f_{\mathbf{k}}) \ln(1 - f_{\mathbf{k}}) + f_{\mathbf{k}} \ln f_{\mathbf{k}}\}.$$

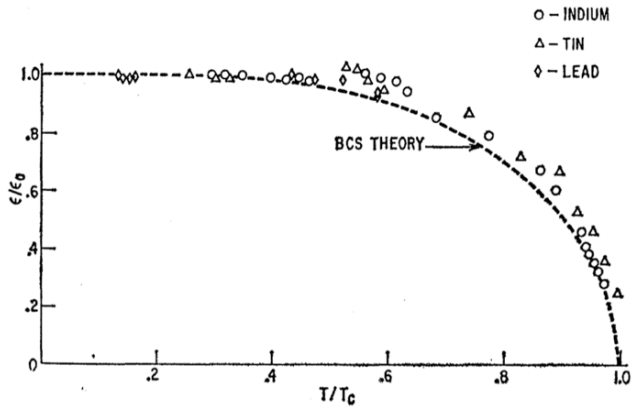
Fig. 2 indicates that the superconducting phase is more ordered compared to its normal phase (12).

## 5. Experimental Verification

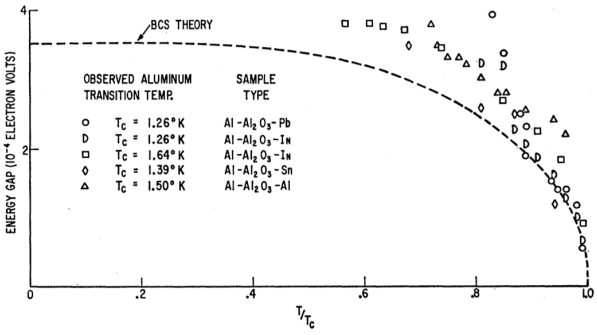
After the theory was proposed, many experiments were designed to test the predictions of superconductors. One such experiment measured the temperature dependence of the energy gap (5), with indium, tin, and lead superconductors as shown in Fig. 3.

The theory predicted that near $T_c$

$$\frac{\Delta(T)}{\Delta(0)} \approx 1.74 \left(1 - \frac{T}{T_c}\right)^{1/2}$$




(a) Conventional superconductors




(b) Aluminum

Figure 3: Indication that the energy gap is temperature dependent (5). (a) Indium, Tin and Lead may then be considered conventional superconductors because their properties may be predicted by BCS theory. (b) Aluminum deviates from the predictions of BCS, and therefore may not be considered a conventional superconductor.

using their mean field approximation, and the assumption that the superconductors were weakly coupled. This assumption did not hold in the case of aluminum superconductors as seen by Fig. 3 from the same study.

The energy gap, the order parameter of the system, manifests itself when calculating the heat capacities of the superconducting state and the normal state. Recall, $C_V = T\frac{dS}{dT}$. Therefore, $\Delta C = C_{\text{es}} - C_{en}$ at $T_c$ gives

$$\Delta C = -N_0 \left(\frac{d\Delta^2}{dT}\right)\bigg|_{T=T_c}.$$

This indicates that the magnitude of the discontinuity of the heat capacity is explicitly dependent on the order parameter $\Delta$. This is best shown by the heat capacities of superconducting aluminum (10) in Fig. 4. Note, $T_c$ for aluminum is 1.163 K.

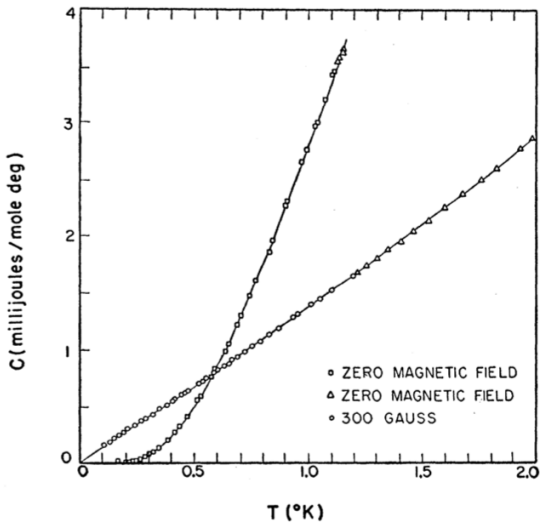



Figure 4: Comparison of heat capacities of superconducting and normal aluminum states (10). For the normal state, the dependence is linear, while it is nonlinear for the superconducting state. The order parameter of the system can be seen clearly at $T_c = 1.163$ K.

## 6. Conclusion

BCS has given the ability to describe microscopically what is occurring in the lattice and Fermi system, and has been verified by many experiments. While we did not address any of the electrodynamics of the superconducting system, the theory does support and is agreement with experimental findings. The flexibility of the BCS theory has allowed for derivative theories that are dependent on the electron-phonon interaction.

There are drawbacks of the theory, as seen by the deviation by the data obtained on the aluminum superconductors. The theory best approximates only conventional weakly coupled superconductors, which aluminum cannot be. From the publication of this theory, there have been discoveries of high $T_c$ superconductors ($T_c > 100$ K), which cannot be explained by BCS.

Many have criticized the theory for being unable to explain the inverse isotope effect, where the $T_c$ is inversely proportional to the isotopic mass, and for not predicting which materials are superconducting. While the theory is a starting point, any deviations from its assumptions, most notably that it is weakly coupled, would not be supported and predict incorrect results. While the theory claims to understand what causes superconductivity, it gives no procedure in choosing which materials would undergo the phase transition. Instead, the results could point to what new types of interactions are occurring within the superconducting system, and use an alternative theory to explain the onset of superconductivity.

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