Beyond BCS

Giorgio Calandra

Physics Engineering, Politecnico di Milano Italy, Milano

Abstract

A small introduction to **BCS theory** is presented in which the most relevant results are reported and introduced. Then, an enhancement of the BCS theory, the Eliashberg theory is presented, trying to focus on the physical improvement of this theory and neglecting the mathematical part. The main part of this paper consists in presenting BCS's limits. They will be listed and the **McMillan's limit** will be discussed. Some numerical computations regarding this limit will be presented as well. The deviation of the **isotope effect** from what is predicted in BCS will be analysed with an example related to YBCO high-temperature superconductor.

---

1. Introduction

In this paper, I will try to talk about superconductivity and, in particular, about the limit of the Bardeen-Cooper-Schrieffer (BCS) Theory to explain the new much-spoken high-temperature superconductors. I will try to do that using the information I found in several papers since there is no unique explanation. My treatment will not focus on the mathematical part for many reasons. First of all, I had not few problems in trying to understand it with no success. Secondly, it will divert the attention from the physics behind certain phenomena which, in my opinion, is the key to trying to understand what is happening. The first part of this paper is dedicated to a brief introduction to BCS theory and to an equally brief introduction to the Eliashberg theory which will be useful in analysing BCS's limits. Before dealing with the more complicated stuff, let's talk shortly about the story of superconductivity. Superconductivity was discovered in 1911 by Kamerlingh Onnes and Holst in mercury at the temperature of liquid helium ($4.2K$). At that time there existed several theories and speculations about the low-temperature behaviour of metals, which ranged from continuously decreasing to unusual upturns, requiring experimental verification. Unexpectedly, liquid mercury showed zero resistance below $4.2K$. Kamerlingh Onnes was awarded the Nobel Prize for Physics in 1913, however, not for the discovery of superconductivity, but for his investigations of material properties at very low temperatures. After demonstrating superconductivity in mercury, a series of metals were measured and found to be superconducting as well, yet only at ultralow temperatures. The highest transition temperature T_C in elemental metals was seen in niobium with a T_C of $9.25K$, quite low indeed. It took almost 50 years until in 1957 a microscopic theory of superconductivity, the so-called BCS theory, was developed. Since the discovery, several superconducting materials have been found with transition temperatures up to $25K$ [1] but never bigger than a certain limit until the end of the '80s. A breakthrough in the field occurred in 1986 when Bednorz and Müller discovered a new class of superconductors, the so-called cuprate high-temperature superconductors with transition temperatures as high as $135K$. They were awarded the Nobel Prize for Physics only one year later, getting the record of the fastest Nobel prize recognition ever. This brought not a few problems to BCS theory that suddenly was found to be incomplete. The exchange mechanism of BCS theory cannot explain the high critical temperature reached in cuprates as I will try to show in the following.

2.   The BCS Theory

The BCS theory of the late 1950s provided an extremely successful framework for understanding superconductors, and in the process gave rise to conceptual breakthroughs which affected the course of physics more broadly for decades to come. The basic insight is that the electrons collectively bind into "Cooper" pairs and simultaneously condense in much the same way as bosons condense into a superfluid state. Cooper pairs are formed during the interaction of two electrons with the vibrations of the lattice. In this process, two electrons exchange a virtual phonon which exists only for a very short time, and which can be emitted by one electron only in the presence of a second electron ready to absorb it. The momentum of the phonon is:

$$|\mathbf{q}| = \frac{\hbar \omega_p}{c_s} \tag{2.1}$$

where ω_p is the frequency of the phonon and c_s the speed of sound. In the exchange, electrons' momentum is conserved:

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_1' + \mathbf{p}_2' \tag{2.2}$$

where $\mathbf{p}_1' = \mathbf{p}_1 - \mathbf{q}$ and $\mathbf{p}_2' = \mathbf{p}_2 + \mathbf{q}$. Furthermore, energy is conserved for the initial and final states. The virtual phonon exists for a very short time which is about $10^{-13}s$ which is one period of the lattice oscillations. In this short period of time, the energy of the system may be different from that of the initial state. This is a consequence of the uncertainty principle $\Delta E \Delta t \simeq \hbar$ between energy and time. If the energy difference between the initial and the intermediate states is smaller than the phonon energy $\hbar \omega_p$, the electron-phonon interaction is attractive [2]. In this picture, we can imagine that a part of the phonon energy contributes to the attractive energy between the two electrons. Due to this attractive interaction, electrons with opposite momenta and spins form the so-called Cooper pairs. Because of the opposite spin, a Cooper pair has a null total spin. This implies that their occupation of energy states must be described by the Bose-Einstein distribution law. Since Cooper pairs are bosons, they all occupy the same quantum state and therefore they all have the same momentum. If, for example, an electric field is applied to the system, Cooper pairs are accelerated through the material but the only scattering processes which lead to a change in momentum are the ones in which Cooper pairs break up. Resistance in the material occurs as soon as the energy taken from the electric field exceeds the binding energy of Cooper pairs. This corresponds to the existence of a critical current density which is perfectly predicted and explained by the theory. In the framework of BCS Theory, all the phenomenological aspects of superconductivity are well predicted, both qualitatively and quantitatively. For example, it is possible to predict a particular quantity related to a peculiar characteristic of superconductors: the energy gap. Assuming that we can express the electron-phonon interaction with a constant V_0, it is possible to see that in the weak coupling limit $g(E_F)V_0 << 1$ the half-width of the energy gap at $T = 0$ is approximate [3]:

$$\Delta(T = 0) \simeq 2\hbar \omega_D \exp\left\{ -\frac{1}{g(E_F)V_0} \right\} \tag{2.3}$$

Here, $g(E_F)$ is the density of states at the Fermi energy and ω_D is the Debye cutoff frequency. But the story does not end here. BCS theory allows us to calculate the transition temperature T_C which, always in weak coupling approximation, results to be [3]:

$$T_C \simeq 1.14 \frac{\hbar \omega_D}{k_B} e^{-\frac{1}{g(E_F)V_0}} \tag{2.4}$$

These two equations imply one of the most astonishing results of BCS. It is possible to get the relationship between the gap energy $\Delta(0)$ and the critical temperature T_C [4]:

$$\frac{\Delta(0)}{k_B T_C} = \frac{2}{1.14} = 1.764 \tag{2.5}$$

I want to stress that these equations are valid in the so-called weak coupling limit which is:

$$g(E_F)V_0 << 1 \tag{2.6}$$

The assumptions made by BCS are essentially exact in this limit. The relevant value, then, is the product $g(E_F)V_0$. When this quantity, named coupling parameter, becomes larger, say 0.2-0.5, we enter the so-called strong coupling regime. This is a key observation to start seeing the limitations of the BCS theory. Fundamental to the BCS mechanism is the fact that, despite the strong direct Coulomb repulsions, the relatively weak attractions between electrons induced by the coupling to the vibrations of the lattice (phonons) can bind the electrons into pairs at energies smaller than the typical phonon energy $\hbar\omega_D$. However, this also implies that the superconducting T_C is always relatively small, as it must satisfy a hierarchy of inequalities [5]:

$$k_B T_C << \hbar\omega_D << E_F \tag{2.7}$$

In some sense, this tells us that the energy of a couple, and thus the critical temperature, is somehow limited by the phonons' energy. This represents a first hint at the limitations of the BCS that we will see in the following. If experimentally one sees that very different energies are involved in the couple formation, this means that the electron-phonon coupling cannot be responsible for such energies and therefore something different must happen. This is the problem that cuprate high-temperature superconductors arose as soon as discovered. Let's now move on and talk about one of the very first enhancements of BCS theory, Eliashberg's theory.

3. BCS Enanchements: Eliashberg Thoery

Eliashberg's Theory is the natural development of BCS theory which includes in its formulation two fundamental aspects:

- The phonon-electron interaction is explicitly considered in the Hamiltonian of the system through appropriate creation and annihilation operators for phonons like the ones used for Cooper pairs in BCS. The Hamiltonian in BCS is said to have "the phonons integrated out" while Eliashberg "integrate them in" [6].

- The retardation effects due to the sluggishness of the phonons response are explicitly included in the equations. This effect is made implicit in BCS with the introduction of the Debye cutoff frequency ω_D.

These enhancements can be seen by looking at the very fundamental equations of BCS and Eliashberg's Theory. The BCS interaction Hamiltonian, in its general form, i.e. with the spin taken into account, is [3]:

$$\mathcal{H}_{int}^{BCS} = \sum_{kk',\sigma\sigma',q} \hbar\omega_q |M_q|^2 \frac{c_{k'-q,\sigma}^* c_{k',\sigma} c_{k+q,\sigma}^* c_{k,\sigma}}{(\varepsilon_k - \varepsilon_{k+q})^2 - (\hbar\omega_q)^2} \tag{3.1}$$

where:

- ω_q is the phonon frequency that will be successively approximated with ω_D.

- ε_k is the energy of the electron with respect to the Fermi level.

- M_q is the matrix element for the electron-phonon interaction which is assumed to be constant. In particular, it is assumed to be independent from the wave vectors k and k'.

- $c_{k,\sigma}$ and $c_{k,\sigma}^*$ are the annihilation and creation operators for an electron with spin σ and wavevector k.

Despite the apparent complexity of this interaction Hamiltonian we notice that the presence of the phonons is only represented by their frequency and the electron-phonon matrix element. Both these two terms will be considered constant in the following calculations in the framework of the standard BCS theory. Instead, the Eliashberg Hamiltonian [6], also in this case by only considering the interaction part, is:

$$\mathcal{H}_{int}^{Hel} = \frac{1}{\sqrt{N}} \sum_{kk'} g(k,k')(a_q + a_{-q}^*)c_{k',\sigma}^* c_{k,\sigma} \tag{3.2}$$

where:

- N is a normalization factor.

- $g(k, k')$ is the electron-phonon coupling function which is, in general, a function of both wave vectors.

- a_q and a_{-q}^* are the annihilation and creation operators for a phonon with wave vector q.

The appearance of the creation and annihilation operators for phonons made the presence of these quasi-particles explicit in the Eliashberg formulation. Moreover, in the expression of the order parameter Φ, which is the phase of the Cooper pairs wave function, a new parameter appears. In a simplified and more physical view, this parameter, called the electron-phonon coupling parameter λ is defined as [6]:

$$\lambda = 2 \int_0^{\omega_D} \alpha^2(\omega_q) F(\omega_q) \frac{d\omega_q}{\omega_q} \tag{3.3}$$

where the term in the integral is the weighted electron-phonon spectral function. In particular, $\alpha^2(\omega_q)$ represents the strength of the interaction, which in general can depend on the phonon frequency, and $F(\omega_q)$ the density of states of phonons [7]. λ roughly corresponds to the $g(E_F)V_0$ term of the standard BCS theory [8]. Thanks to this term, Eliashberg's theory is capable of keeping into account explicitly the retardation effects connected to the spectral distribution of phonons. Thanks to this formulation it is possible to keep into account the strong coupling effect that BCS is not capable of treating.

4. BCS Limits

I decided to briefly talk about Eliashberg's theory because it was used by McMillan [8] to derive the so-called McMillan limit for the critical temperature of a superconductor. This derivation was made in 1967, far before the discovery of the cuprate high-temperature superconductor. However, after the formulation of the BCS theory in 1957 scientists started to prove the theory, studying different and different materials and confronting the results with the prediction of the theory. It was clear from the beginning that not all superconductors can be explained by BCS theory. We call conventional superconductors the ones which can be explained by BCS and unconventional the ones which cannot. The challenges encountered by BCS can be summarized in three points:

- **Isotope Effect**: BCS predicts that the critical temperature is inversely proportional to the square root of the atomic mass of the ions which compose the metal. Which means: $T_C \propto M^{-\alpha}$ with α, which is called isotope coefficient, equal to $1/2$. Not all superconductors, either elemental or non-elemental, have such a coefficient. For example, the experimental data about the isotope effect for transition metals is not well explained by BCS [9].

- **Cuprate superconductors**: this is one of the most difficult challenges of superconductivity in general which made clear the inadequacy of the BCS theory to explain such a phenomenon. Experiments made clear that the formation of Cooper pairs in these materials cannot be explained in terms of electron-phonon interaction. Nowadays scientists are trying to find a modified version of the BCS theory in which the coupling which forms the electron pairs is not the interaction with a phonon but, for example, with polarons or magnons. Then, after finding a new medium for the interaction, BCS can still be considered valid. There is no consensus on this topic.

- **Iron-based superconductors**: this new class of material was recently discovered. They exhibit high critical temperatures which cannot be explained in the context of BCS [2].

I will focus my attention on the first two points of this list, trying to see whether there exists or not an answer to these problems in the framework of BCS.

5. McMillian Limit

It is worth noting that the very much spoken high-temperature superconductors (non-cuprates) do not represent a problem for the temperature in itself. The problem arises with cuprate because they exhibit a high critical temperature under normal pressure conditions. In fact, BCS predicts that the critical temperature depends on the phonon frequency and this latter parameter changes

with pressure. In particular, the higher the pressure, the higher the frequency of the lattice vibrations, the higher the critical temperature. However, going back to the BCS problems, the first question one may ask is whether or not there exists a limit on the critical temperature of superconductors in the scheme of BCS. Well, the answer is yes and no. The standard BCS theory does not include limitation of the critical temperature as we can see from the expression of T_C [4]:

$$T_C = 1.14 \frac{\hbar \omega_D}{k_B} \exp\left\{-\frac{1}{\lambda}\right\} \tag{5.1}$$

where I substitued $g(E_F)V_0 = \lambda$. Nevertheless, it is often said that based on BCS theory, the T_C of a conventional superconductor cannot exceed $40K$ [8]. However, this limit, which is the so-called McMillan limit, does not come from the standard BCS theory since McMillan derived it using a linearisation of the Eliashberg equations. In particular, McMillan derived an expression for the critical temperature valid both in strong coupling and weak coupling regimes. The formula can be derived from Eliashberg's theory by using numerical integration and results in:

$$T_C = \frac{1}{1.45} \frac{\hbar \omega_D}{k_B} \exp\left\{\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right\} \tag{5.2}$$

where μ^* is called Coulomb pseudopotential and physically represents the (reduced) residual Coulomb repulsion experienced by a Cooper pair [7]. In the BCS theory, this term is not considered, i.e. $\mu^* = 0$, and it is easy to verify that in weak coupling ($\lambda << 1$) and with $\mu^* = 0$ the equation found by McMillan simply resembles the one found in the standard BCS (Eq.(5.1)). Based on my reading of several articles, at the state of the art, there is no a priori calculation to predict the value of μ^* and this is usually computed through experimental data. After computing the critical temperature, McMillan proceeded with his analysis trying to find a more physical form for the electron-phonon coupling constant λ. He found:

$$\lambda = 2 \int_0^{\omega_D} \alpha^2(\omega_q) F(\omega_q) \frac{d\omega_q}{\omega_q} = \frac{g(E_F)\langle \mathfrak{g}^2 \rangle}{M \langle \omega^2 \rangle} \tag{5.3}$$

where:

- $g(E_F)$ is the electronic density of state at the Fermi energy.

- M is the mass of the ions.

- $\langle \omega^2 \rangle$ is the average of the square of the phonon frequency.

- $\langle \mathfrak{g}^2 \rangle$ is the square of a matrix element which expresses the electron-phonon interaction. It is the analogous of the matrix element $|M_q|$ we saw in the BCS Hamiltonian (Eq.(3.1)). Dimensionally, $\mathfrak{g}$ is an electronic quantity with units of energy/length.

This result makes the physical meaning of the coupling constant λ a bit more clear. It is proportional to the strength of the electron-phonon interaction and it increases with the number of electrons at the Fermi surface which are the ones available for the Cooper pairs formation. λ decreases with the mass of the ions, which limits the frequency of the oscillation. Moreover, in this form, λ resembles the BCS-like expression for which $\lambda = g(E_F)V_0$ with V_0 playing the role of the matrix element. McMillan, then, moves on with an empirical observation. In particular, he wanted to calculate from experimental data the value of the matrix element $\langle \mathfrak{g}^2 \rangle$ by rearranging the previous formula:

$$\langle \mathfrak{g}^2 \rangle = \frac{\lambda M \langle \omega^2 \rangle}{g(E_F)} \Rightarrow \langle \mathfrak{g}^2 \rangle g(E_F) = \lambda M \langle \omega^2 \rangle \tag{5.4}$$

By looking at the data in Tab.1, which were the experimental data known at that time, he found a remarkable result. For the BCC transition metals the product $\langle \mathfrak{g}^2 \rangle g(E_F)$ is constant within the experimental error and it is worth about $\sim 7eV/\text{Å}^2$. McMillan said [8] that "we have at present no theoretical explanation of this fact; we have only empirical observation for these five bcc transition metals". A better look at Tab.1 makes us realize that also for another class of materials (Al, In, Pb) the product between the density of state and the matrix element is constant. This class is the
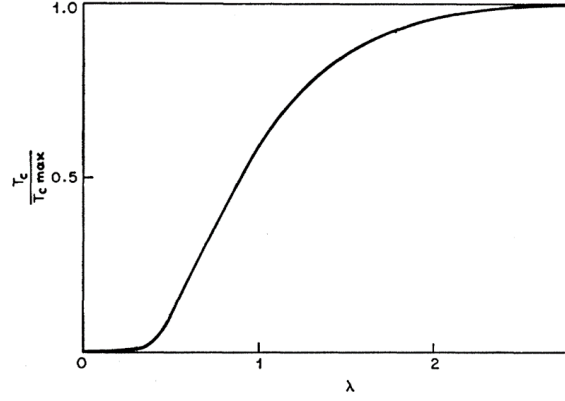
Figure 1: The superconducting transition temperature according to Eq.(5.2) with $\mu^* = 0.13$, assuming that the coupling constant obeys Eq.(5.6) from [8].

one of polyvalent metals for which $\langle \mathfrak{g}^2 \rangle g(E_F) \sim 2eV/\text{Å}^2$. In this case, McMillan managed to find a theoretical explanation for the constantness of this product even if with some approximations. Nevertheless, he used these observations to write $\lambda M \langle \omega^2 \rangle = C$ where C is an appropriate constant for a given class of materials. With this conclusion, we can move to the study of an upper limit for the critical temperature. McMillan rewrote a simplified formula for the critical temperature of Eq.(5.2) considering a zero Coulomb pseudo potential ($\mu^* = 0$):

$$T_C \simeq \langle \omega \rangle \exp\left\{ -\frac{1+\lambda}{\lambda} \right\} \tag{5.5}$$

He then used the experimental observation for which:

$$C = \lambda M \langle \omega^2 \rangle \Rightarrow \lambda = \frac{C}{M \langle \omega^2 \rangle} \tag{5.6}$$

and he substituted this into the critical temperature expression:

$$T_C \simeq \langle \omega \rangle \exp\left\{ -\left[\frac{M \langle \omega^2 \rangle}{C} + 1 \right] \right\} \tag{5.7}$$

By minimizing this expression with respect to $\langle \omega \rangle$ one finds:

$$\frac{dT_C}{d\langle \omega \rangle} = 0 \Rightarrow \langle \omega \rangle = \sqrt{\frac{C}{2M}} \tag{5.8}$$

which corresponds to $\lambda = 2$. The maximum critical temperature corresponding to this maximum point is:

$$T_C^{max} = \left(\frac{C}{2M} \right)^{1/2} e^{-3/2} \tag{5.9}$$

In its work, McMillan reported the graph of the ratio T_C/T_C^{max} calculated using the precise expression of the temperature of Eq.(5.2) and not the simplified expression. The graph is shown in Fig.1. This function shows a broad maximum at $\lambda \simeq 2$ and falls off sharply for $\lambda < 1$. McMillan in its work does not report the details of this precise calculation. Therefore, I decided to use Matlab to compute the exact maximum of the critical temperature of Eq.(5.2). The result are shown in the Appendix. Then, I decided to use the simplified expression of the maximum critical temperature to compute it for the elements of Tab.1. Before proceeding it is worth noting that as a habit of theoretical physicists, McMillan did not put any constant, such as $\hbar$ or k_B, in its expressions. The complete formula is therefore:

$$T_C^{max} = \frac{\hbar}{k_B} \left(\frac{C}{2M} \right)^{1/2} e^{-3/2} \tag{5.10}$$

Table 1: Empirical values of the average electronic matrix element $\langle \mathfrak{g}^2 \rangle$, $g(E_F)$ from [8].

Metal	$g(E_F)$ (states/eV)	$\langle \mathfrak{g}^2 \rangle$ (eV^2/Å^2)	$g(E_F)\langle \mathfrak{g}^2 \rangle$ (eV/Å^2)
V	1.31	3.5	4.6
Nb	0.91	7.9	7.2
Ta	0.77	7.9	6.1
Mo	0.275	24.6	6.8
W	0.148	42.5	6.3
Al	0.206	9.7	2
In	0.21	8.4	1.76
Pb	0.3	7.8	2.34
V$_3$Si	2.33	4.9	11.3

My results are reported in Tab.2. The table confirms, at least for these few elements, what has been told at the beginning of this section: for a conventional superconductor, the critical temperature seems to be limited up to a certain value, smaller than $40K$. These values differ from the more accurate one computed by using Eq.(5.2) with a Coulomb pseudopotential $\mu^* \neq 0$ but at least they give an idea of the utility of McMillan's equation. For more precise calculations see Appendix. Unfortunately, although quite simple in principle this is not the answer we were looking for. Quite fun is that while I was studying, trying to understand McMillan's mathematics and steps, I read by mistake an article that seems to disprove McMillan's work. In the beginning, I was desperate since as soon as I was starting to understand something, suddenly everything seemed to be lost but in the end, it would have been worse to not know it and also, science works like this. McMillan limit has been at the center of quite a dispute between scientistic for some time. It took some years until Allen and Dynes [11] in 1975 managed to completely disprove McMillan's limit. In particular, they based their work on the information retrieved through the neutrons scattering technique used to determine the shape of the electron-phonon spectral function $\alpha^2 F(\omega)$. They used an Einstein model-like expression for $F(\omega)$, i.e. a Dirac Delta function, and they developed a more accurate analysis for the temperature. Their results can be summarised as follows:

- For large values of λ the critical temperature T_C scales at least as fast as $\lambda^{1/2}$ rather than saturating as occours in McMillans formulas.

- They found that T_C is bounded from below if λ is large.

- In the range $0.3 < \lambda < 1.5$ their calculated T_C agrees very well with McMillan's functional form.

The numerical result of Allen and Dynes computations can be seen on the left side of Fig.2. On the right side of Fig.2 some experimental results from [11] are reported. These results show the

Table 2: Maximum critical temperature for some metals computed by using Eq.(5.10). The values for C and T_C come from [8] and the value for the atomic mass M from [10].

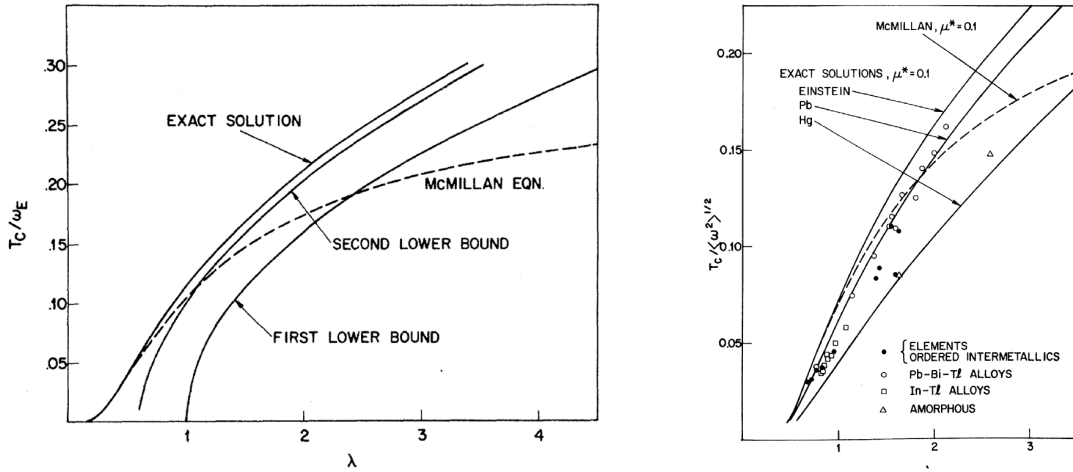| Metal	C (eV/Å^2)	C (J/m^2)	M (10^{-26}kg)	T_C (K)	$T_C^{\max}$ (K)
V	4.60	73.6	8.46	5.3	35.5
Nb	7.20	115.2	15.4	9.22	32.9
Ta	6.10	97.6	30.1	4.48	21.7
Mo	6.80	108.8	15.9	0.92	31.5
W	6.30	100.8	30.5	0.012	21.9
Al	2.00	32.0	4.48	1.16	32.2
In	1.76	28.2	19.1	3.4	14.6
Pb	2.34	37.4	34.4	7.19	12.6
V$_3$Si	11.3	180.8	30.0	17	29.6

Figure 2: The solid curves are calculated from the various shapes of $\alpha^2 F$ shown in Fig.3 and with $\mu^* = 0.1$. The dashed curve is the McMillan equation using $\mu^* = 0.1$ and a modified prefactor. The experimental points are taken from tunnelling data reported in [11].

exact solutions computed with three different shapes of the phonon density of states: the Dirac-Delta Eistein shape theoretically computed and the exact experimental densities of state for Pb and Hg as shown in Fig.3. Allen and Dynes [11], conclude their work stating that McMillan's "$\lambda = 2$ *limit is spurious*" since it relays on an extrapolation which fails for $\lambda > 1$. In conclusion, despite McMillan's work bringing a little bit of hope in understanding the limitation of BCS for high-temperature superconductivity, the following work of Allen and Dynes confirms that there is no theoretical limitation to the critical temperature in the BCS framework.

6.   Isotope Effect

The other challenge encountered by BCS was the explanation of the isotope effect for some classes of materials. The isotope effect in superconductors refers to the change in the critical temperature of a superconducting material when its isotopes are substituted, i.e. when the atomic mass M changes. It is easy to see in which way BCS explain this dependence of T_C on M:

$$T_C \propto \omega_D \propto M^{-1/2} \tag{6.1}$$

This $1/2$ value is called the isotope exponent and it is denoted with α. The agreement between the expected $M^{-1/2}$ dependence and experiment is very good for example in the case of Sn [4]. However, particularly for the transition metals considerable deviation from $1/2$ occurs for the isotope exponent. In Os, for example, the isotope exponent is 0.10 ± 0.10 or in Mo it is 0.37 ± 0.07 [9]. Not only this, there are some other metals, such as Zr, in which the isotope effect completely vanishes [8], i.e. $\alpha = 0$. Niobium alloys are other materials which significantly deviate from the isotope effect. These deviations are not surprising when one recalls that within the BCS theory, the Debye frequency ω_D is the only quantity which contains information about the material's spectrum [4]. In general, to better talk about the isotope effect is appropriate to define precisely the isotope coefficient α. One would guess that since $M^\alpha T_C = cost$ then $\alpha = -\ln T_C / \ln M$. However, since the range of variation of M and T_C is very small, one defines the isotope exponent (or coefficient) equivalently [12]:

$$\alpha \equiv -\frac{d \ln T_C}{d \ln M} \tag{6.2}$$

In the standard BCS, and also in the standard Eliashberg theory, this coefficient is always equal to $1/2$. There are two clear sources of deviation from $\alpha = 1/2$ [7]:

- Non-elemental superconductors. In these superconductors made by more than one element, the isotopic substitution for one of the elements will result in varying T_C depending on
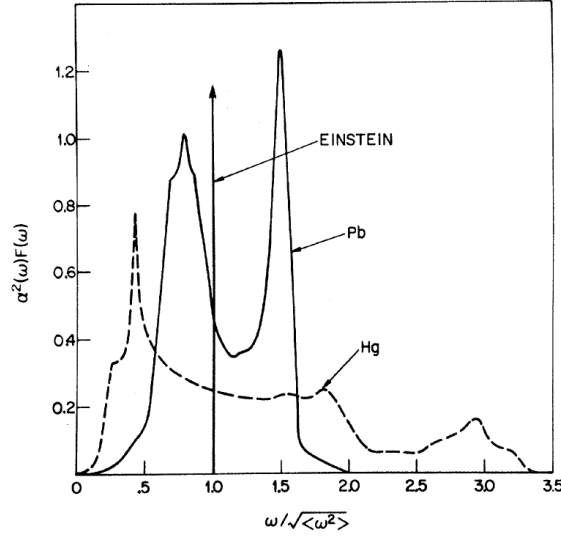
Figure 3: Electron-phonon spectral function $\alpha^2 F$ measured by tunneling experiment as reported in [11].

how the element which has been substituted contributes to the important phonon modes of the material. In this case, it is more appropriate to define a partial isotope coefficient $\alpha_i = -d \ln T_C / d \ln M_i$ where M_i is the mass of the ith element. Then, one can get the total isotope coefficient summing over all the i and it will sum to $1/2$ [7].

- Non-zero Coulomb pseudopotential. Let's start repeating what has been told in Sec.5: BCS theory does not consider the presence of this term which means $\mu^* = 0$. However, if we think about the fact that the Coulomb pseudopotential represents the residual Columb interaction between electrons in a Cooper pair, we can understand how this affects the critical temperature and therefore the isotope effect behaviour. The higher the residual repulsion, the smaller the influence of the phonon energy on the Couple, and the smaller the dependence on the isotope masses. Therefore, we expect that the presence of μ^* reduces the isotope exponent. Using the definition of the isotope exponent Eq.(6.2), one can derive from McMillan's critical temperature equation Eq.(5.2) the following expression [7]:

$$\alpha = \frac{1}{2}\left(1 - \frac{1.04(1+\lambda)(1+0.62\lambda)}{[\lambda - \mu^*(1+0.62\lambda)]^2}\mu^{*2}\right) \tag{6.3}$$

From this equation, it is easy to see that α reduced to $1/2$ when $\mu^* = 0$ (BCS value) and that in general $\alpha < 1/2$ when $\mu^* \neq 0$, regardless of its sign.

I decided to introduce the last equation because it is helpful to analyze an interesting example. The discovery of high-temperature cuprate materials prompted considerable activity concerning the isotope coefficient. The first cuprate high-temperature superconductor to have ever been observed was the very famous YBCO ($YBa_2Cu_3O_{7-y}$). In this and other cuprates, the isotope coefficient displays some unusual doping dependence but it is essentially zero in the optimally doped YBCO with a critical temperature of $90K$ [7]. The question that now arises is: "Can a realistic and conventional electron-phonon interaction give rise to a $90K$ superconductor with a near-zero isotope coefficient?". We want to use McMillan's theory to try to get a qualitative answer to this question. In particular, we will use the equation for the isotope coefficient seen before (Eq.(6.3)) and the one for the critical temperature (Eq.(5.2)), which I report here for convenience:

$$T_C = \frac{1}{1.45}\frac{\hbar\omega_D}{k_B}\exp\left\{\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}$$

$$\alpha = \frac{1}{2}\left(1 - \frac{1.04(1+\lambda)(1+0.62\lambda)}{[\lambda - \mu^*(1+0.62\lambda)]^2}\mu^{*2}\right)$$
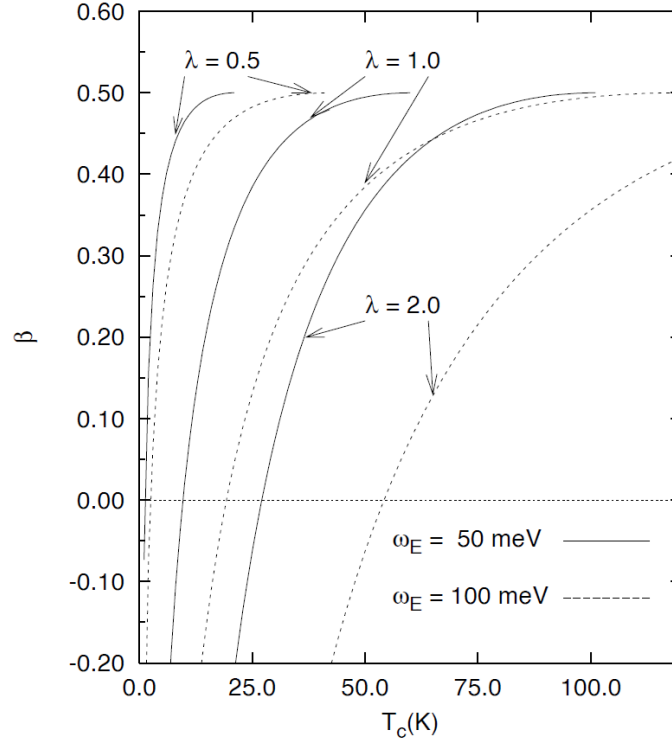
Figure 4: The isotope coefficient α vs. T_C from [7]. Along each curve T_C changes because the Coulomb pseudopotential μ^* is being varied.

For a given electron-phonon coupling, λ, and phonon frequency ω_D, one can determine the required value of μ^* to fix T_C from the first of these two equations. Then, one can use these parameters to determine the isotope coefficient, α, through the second equation. Such a procedure was done by [7] and the results are plotted in Fig.4. These results show that a low value of α is difficult to attain with high T_C. On the other hand, for low T_C materials, it is not that difficult to obtain a low isotope coefficient, zero too. To obtain the desired results for optimally doped $YBa_2Cu_3O_{7-y}$ ($T_C \simeq 90K$ and $\alpha \simeq 0$) would require high-frequency phonons $\omega_D \simeq 100meV$ with very strong electron-phonon coupling $\lambda \simeq 5$. That such a coupling strength is unrealistic, particularly for such very high-frequency phonons, was discussed much earlier by Cohen and Anderson [13]. In summary, the conventional Eliashberg theory (and McMillan equations derived from it) can yield a near-zero isotope coefficient, provided T_C is low (see Fig.4). One must go beyond the conventional BCS framework to obtain a zero isotope coefficient with a high critical temperature such as the one for YBCO ($T_C \simeq 90K$).

7.   Conclusion

The scope of this work was to critically analyse the limit of BCS theory in explaining the physics and the "numbers" of high-temperature superconductors. This has been done in a simplified but physical way. I tried to show that working in the frame of BCS, even with some enhancements of the theory, it is not possible to predict and explain the high-temperature superconductivity phenomenon. In part, this has been shown with the McMillan equations which, despite not being valid for all materials, i.e. for all λ, shows that BCS has some sort of limits in the temperature which is in fact not respected by these new classes of superconductors. The confutation of McMillan's work by Allen and Dynes seems to bring a little hope in the BCS limitations since a not-limited critical temperature could make things work also in the BCS scheme. The final blow to the standard BCS's hopes of explaining high-temperature superconductors is given by the isotope effect. Apart from all the experimental deviation from the 1/2 isotope coefficient, it has been shown the high temperature and the deviation from the standard isotope effect cannot be explained in terms of a conventional electron-phonon interaction as predicted by BCS's Theory.

A.   Matlab Code

I implemented a Matlab script to find the maximum of McMillan Eq.(5.2) with a Coulomb pseudopotential $\mu^* = 0.13$ for BCC transition metals, i.e. $C \simeq 7eV/\text{Å}^2$. The code is the following.

```matlab
clear
close all
format long

%% Constants defintion
hbar = 1.05459*10^(-34); %Js
kB = 1.380649*10^(-23); %J/K
mu = 0.13;
C = 94; %J/m^2
M = 10^(-26); %kg


A = (1/1.45)*(hbar/kB)*sqrt(C/M);

%% Function definition
syms X           % X plays the role of lambda
Tc = A*sqrt(1/X)*exp((-1.04*(1+X))/(X-mu*(1+0.62*X)));

%Tc_dev = eval(['@X' char(diff(Tc(X)))]);
Tc_dev = matlabFunction(diff(Tc, X), 'Vars', {X});

%% Minimum
% Define the objective function to minimize
Tc_numerical = @(X) -double(subs(Tc, X)); % to convert Tc into
    numerical value

% Initial guess for the minimum
X0 = 1.0;

% Call fminsearch to find the minimum
[X_max, Tc_max] = fminsearch(Tc_numerical, X0);
Tc_max=-Tc_max;

% Display the results
fprintf('Minimum found at X = %f\n', X_max);
fprintf('Minimum value of Tc = %f\n', Tc_max);

%% Normalization
f= Tc/Tc_max;

%% Graph of Tc
figure
fplot(f,[0, 5]);
xline (X_max, 'g');
ylim([0, 1]);
```

The results are:

```
>>
Minimum found at X = 2.858008
Minimum value of Tc = 62.507586
```

The graph is shown in Fig.5. This is the exact graph found by McMillan (see Fig.1). The broader x-axis also shows that the critical temperature decreases for λ greater than λ_{max}. After this, I computed the exact values of the maximum critical temperature using the precise values of C and M to see the difference from the approximated ones of Tab.2. The code used to do that is:
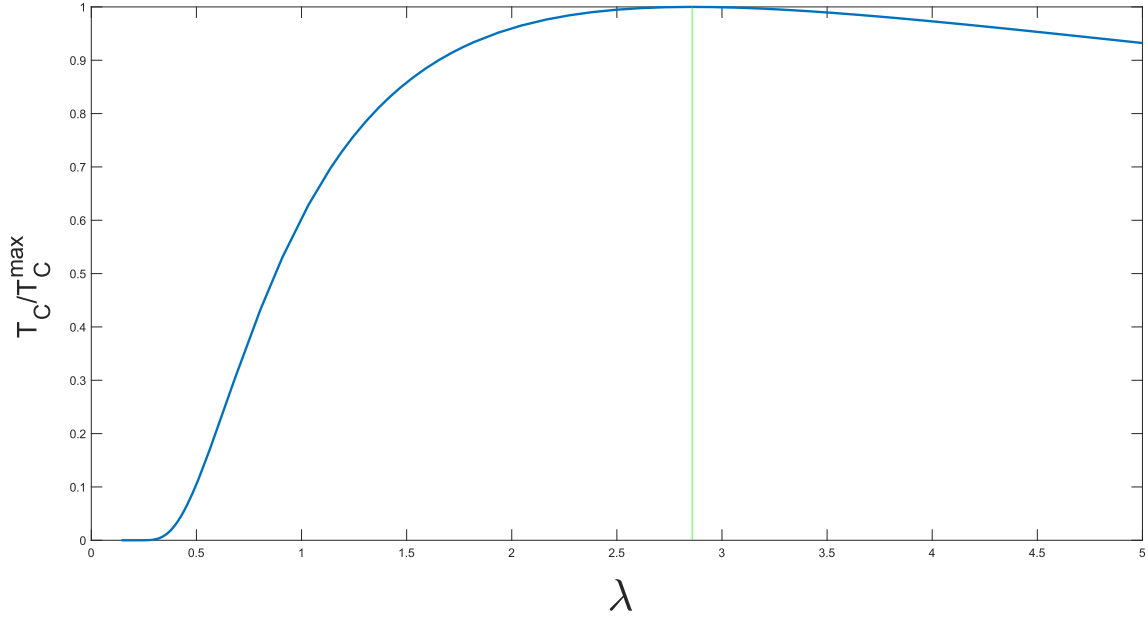
Figure 5: The superconducting transition temperature according to Eq.(5.2) with $\mu^* = 0.13$, assuming that the coupling constant obeys Eq.(5.6) from [8] computed through Matlab.

```matlab
%% Listing all the variables
C_list = [73.6; 115.2; 97.6; 108.8; 100.8; 32; 28.16; 37.44;
    180.8]; %J/m^2
M_list = [8.45879E-26; 1.54281E-25; 3.00392E-25; 1.59329E-25;
    3.05207E-25; 4.48014E-26; 1.9063E-25; 3.44064E-25; 3.00408E-25];
    %kg

%% Max Tc computation
syms X
Tc_max_list = zeros(length(C_list), 1);
for i=1:length(C_list)
    A= (1/1.45)*(hbar/kB)*sqrt(C_list(i)/M_list(i));
    Tc = A*sqrt(1/X)*exp((-1.04*(1+X))/(X-mu*(1+0.62*X)));
    Tc_numerical = @(X) -double(subs(Tc, X)); % to convert Tc into
        numerical value
    [X_max, Tc_max] = fminsearch(Tc_numerical, X0);
    Tc_max_list(i)=Tc_max;
end
```

The difference between the exact result and the approximated one can be estimate as follows:

```matlab
    %% Max Tc approx and errors
Tc_max_list_approx = zeros(length(C_list), 1);
a_error = zeros(length(C_list), 1);
r_error = zeros(length(C_list), 1);

for i=1:length(C_list)
    A_approx = (hbar/kB)*sqrt(C_list(i)/(2*M_list(i)));
    Tc_max_approx = A_approx*exp(-3/2);
    Tc_max_list_approx(i)=Tc_max_approx;
    a_error(i) = Tc_max_list(i)-Tc_max_list_approx(i);
    r_error(i) = a_error(i)/Tc_max_list(i);
end
```

Which gives a constant relative error of about 50%. This suggests that is probably better to rewrite the maximum critical temperatures of Tab.1 using the exact data. Both the exact values and the approximated one for T_C^{max}, as well as T_C and errors, are reported in Tab.3.

Table 3: Summary of the values for the maximum critical temperatures of some metals with their exact transition temperatures from [8].

Metal	$T_C^{\mathrm{max,\ exact}}$ (K)	$T_C^{\mathrm{max,\ approx}}$ (K)	T_C (K)	e_a (K)	e_r (%)
V	23.1	35.5	5.3	12.5	53.9
Nb	21.4	32.9	9.22	11.5	53.9
Ta	14.1	21.7	4.48	7.6	53.9
Mo	20.5	31.5	0.92	11.0	53.9
W	14.2	21.9	0.012	7.7	53.9
Al	20.9	32.2	1.16	11.3	53.9
In	9.5	14.6	3.4	5.1	53.9
Pb	8.2	12.6	7.19	4.4	53.9
V_3Si	19.2	29.6	17	10.4	53.9

[14] [15] [16]

References

[1] Annette Bussmann-Holder and Hugo Keller. "High-temperature superconductors: underlying physics and applications". In: *Zeitschrift für Naturforschung B* 75.1-2 (Oct. 2019), pp. 3–14. DOI: 10.1515/znb-2019-0103. URL: https://doi.org/10.1515%2Fznb-2019-0103.

[2] R. Wesche. *Physical Properties of High-Temperature Superconductors*. United Kingdom: Wiley, 2015. ISBN: 9781119978817.

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. "Theory of Superconductivity". In: *Phys. Rev.* 108 (5 Dec. 1957), pp. 1175–1204. DOI: 10.1103/PhysRev.108.1175. URL: https://link.aps.org/doi/10.1103/PhysRev.108.1175.

[4] H. Ibach and H. Lüth. *Solid-state physics*. Berlin: Springer, 2003.

[5] B. Keimer et al. *High Temperature Superconductivity in the Cuprates*. 2014. arXiv: 1409.4673 [cond-mat.supr-con].

[6] F. Marsiglio. "Eliashberg theory: A short review". In: *Annals of Physics* 417 (June 2020), p. 168102. DOI: 10.1016/j.aop.2020.168102. URL: https://doi.org/10.1016%2Fj.aop.2020.168102.

[7] F. Marsiglio and J. P. Carbotte. *Electron - Phonon Superconductivity*. 2001. arXiv: cond-mat/0106143 [cond-mat.supr-con].

[8] W. L. McMillan. "Transition Temperature of Strong-Coupled Superconductors". In: *Phys. Rev.* 167 (2 Mar. 1968), pp. 331–344. DOI: 10.1103/PhysRev.167.331. URL: https://link.aps.org/doi/10.1103/PhysRev.167.331.

[9] James W. Garland. "Isotope Effect in Superconductivity". In: *Phys. Rev. Lett.* 11 (3 Aug. 1963), pp. 114–119. DOI: 10.1103/PhysRevLett.11.114. URL: https://link.aps.org/doi/10.1103/PhysRevLett.11.114.

[10] *Periodic Table - Zanichelli*. URL: https://tavolaperiodica.zanichelli.it/it/thematic-tables/atomic-mass/23.

[11] P. B. Allen and R. C. Dynes. "Transition temperature of strong-coupled superconductors reanalyzed". In: *Phys. Rev. B* 12 (3 Aug. 1975), pp. 905–922. DOI: 10.1103/PhysRevB.12.905. URL: https://link.aps.org/doi/10.1103/PhysRevB.12.905.

[12] Jules de Launay. "The Isotope Effect in Superconductivity". In: *Phys. Rev.* 93 (4 Feb. 1954), pp. 661–665. DOI: 10.1103/PhysRev.93.661. URL: https://link.aps.org/doi/10.1103/PhysRev.93.661.

[13] D H Douglass. "Superconductivity in d- and f-band metals". In: (Jan. 1976), p. 17.

[14] J.W. Rohlf. *Modern Physics from alpha to Z0*. Wiley, 1994. ISBN: 9780471572701. URL: https://books.google.it/books?id=x5trQgAACAAJ.

[15] Emanuel Maxwell. "Isotope Effect in the Superconductivity of Mercury". In: *Phys. Rev.* 78 (4 May 1950), pp. 477–477. DOI: 10.1103/PhysRev.78.477. URL: https://link.aps.org/doi/10.1103/PhysRev.78.477.

[16] C. A. Reynolds et al. "Superconductivity of Isotopes of Mercury". In: *Phys. Rev.* 78 (4 May 1950), pp. 487–487. DOI: 10.1103/PhysRev.78.487. URL: https://link.aps.org/doi/10.1103/PhysRev.78.487.