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Bachelor thesis

SUPERCONDUCTIVITY IN REAL SPACE

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Abstract

The illustrations that are commonly used to explain electron behaviour in superconductors are flawed. A purely mathematical approach on the other hand gives limited insight. This thesis derives a visualization of the Cooper pair that is valid within the BCS model: a circular movement of the electrons seems to be the only way to sustain the attractive potential.

It is then demonstrated that an alternative model can also lead to the BCS equations. Such a model is derived from the third law of thermodynamics: The formation of a Wigner crystal seems to maximize the ordering of electrons in the ground state. The presence of superconductivity in such a structure is believed to be the result of local phase coherence.

The two models are compared and the differences are emphasised. Experiments to find the correct model are proposed, based on these differences.

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1. Introduction

This bachelor thesis investigates the structure and movement of electrons in a superconductor in real spatial dimensions. This chapter introduces the topic of superconductivity and motivates why it is useful to study it in real space.

This thesis is written in such a way that its essence should be understandable without understanding the equations.

A list of symbols has purposefully been left out, since the author believes that it improves the readability when symbols are defined right before or after the equations that use them.

1.1. Superconductors

Superconducting materials have no measurable resistance and they screen out magnetic fields. They only become superconducting when they are cooled below their critical temperature T_c, which for all known superconductors is far below 0 degrees Celsius. Below this temperature the superconductivity can still be destroyed by applying a critical field H_c or a critical current density J_c.

Superconductors have a fascinating history and some remarkable applications. These will be discussed in chapter 2.

1.2. Visualizing superconductivity

The analysis of superconductivity usually involves something like 'quasi-particles exchanging virtual phonons in reciprocal space', making it hard, if not impossible to visualize the behaviour. Reciprocal space is discussed in chapter 2 and the meaning and origin of the other terms will be explained in chapter 4.

However, even then, this will remain a very abstract way of dealing with physics. Such an abstract approach, often based on pure formalism, is not uncommon in theoretical physics; It often leads to correct results, but it also creates a tendency to lose touch with physical reality. An analysis of real particles in real space may lead to a better understanding of superconductivity and electron behaviour in general.

Superconductivity is often explained using a picture of two electrons (a Cooper pair), where one follows the other: The negative charge of the first electron attracts the positive ions. In this way it leaves a positive trail, that attracts the second electron. This mechanism is represented in figure 1.1. The grey dots represent the ions. Anderson gives the impression that this picture originates from him [2].

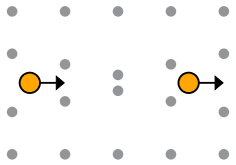


Figure 1.1.: Common representation of a Cooper pair

It is however known that this picture is incorrect[1]. The use of this picture in textbooks and courses may be misleading and it is probably a good idea to replace it with a representation that is physically correct. Realistic pictures can increase the accessibility of the field of superconductivity and they might even lead to new insights.

Using a picture that is valid within the approximations of the ruling BCS theory (which is introduced in chapter 2) should clarify the mechanisms on which this theory is based. Chapter 4 presents such a real space visualization of the Cooper pair, that is valid within the assumptions of BCS theory.

1.3. Alternative models

The validity of this representation will be limited by the validity of the BCS theory itself. It is known that the equations from this theory are correct for a large group of superconductors, but the requirements to get these equations are limited (as will be discussed in chapter 3) and could be met by other models.

Such a model is discussed in chapter 5. It will be derived from a fundamental law in physics and an explanation is given for the origin of superconductivity in this model.

Chapter 6 discusses both the visualization of the BCS model and the alternative model. The differences between the models are emphasised and used as a basis to propose experiments that might be able to determine which theory is correct.

Finally, chapter 7 will draw conclusions and give recommendations for further research.

1.4. Research objectives

The research objectives of this project can be summarized as:

1. Visualize electron behaviour according to the ruling BCS theory.
2. Investigate the theoretical validity of an alternative model.

The first objective will be treated in chapter 3 and 4; Chapter 5 and 6 deal with the second objective. But first, chapter 2 will give some background information on superconductivity and real space.

[1] The electrons should for example move in opposite directions

2. BACKGROUND

The title of this thesis is 'Superconductivity in real space'. To properly understand this thesis it is essential to know the full meaning of both 'superconductivity' and 'real space'.

This chapter will give the appropriate background information. The first section discusses the historical and theoretical aspects of the development of superconductivity. The second section explains the meaning of real space and its relation to other spaces, such as reciprocal space.

2.1. THE DEVELOPMENT OF SUPERCONDUCTIVITY

The main focus of this thesis is the microscopic theory of superconductivity, which will be discussed in chapter 3. Phenomenological theories and macroscopic currents will only be mentioned. Even Abrikosov vortices (microscopic current loops in superconductors) will not be discussed beyond this chapter.

However, for a more complete understanding, it is useful to place the microscopic theory in the context of the total development of superconductivity. Therefore we will now also discuss the other theories that played an important role in understanding superconductivity. They will not be discussed in much detail, but it is important to know their results and historical context.

For a more complete discussion it is recommended to read a textbook on this subject [3, 4, 5]. Derivations for most of the equations can be found in appendix A.

2.1.1. EXPERIMENTS

The story of superconductivity started in 1911 when Kamerlingh Onnes discovered it in his experiments with liquid helium [6]. His discovery was pure experimental and it took a lot of time for theoreticians to catch up.

In the early days of superconductivity new insights came only from experiments. In 1933 these experiments lead to the discovery of the Meissner effect[7]: the expulsion of magnetic fields from a superconductor. In 1950 experiments led to the discovery of the isotope effect: it was found that the critical temperature of superconductors is proportional to the isotopic mass of the atoms.

$$T_c \propto \frac{1}{\sqrt{M}} \tag{2.1}$$

In the early period many scientists tried to explain superconductivity, but even great scientists such as Einstein and Feynman failed in their attempts [8]. It took several decades for the first useful theory to appear and a theory on the microscopic processes had to wait almost half a century.

In the mean time the amount of theories kept growing, so that at a certain point it became even necessary to classify the various theories in groups. These three groups were: 'the hypothesis of spontaneous current', 'the diamagnetic hypothesis' and the 'quasi-microscopic method in the theory of superconductivity'[9]

2.1.2. London theory

The first successful theory of superconductivity was presented by the London brothers in 1935[10]. They used a two fluid-model, which states that there is a fluid of normal electrons, that one by one[1] change into 'super electrons' that form a second fluid, as the temperature drops further below the critical temperature. These super electrons have no resistance, which leads to a simple response to fields. The resulting equations, known as the London equations, are given here.

$$E = \Lambda \frac{dj_s}{dt} \tag{2.2}$$

$$B = -\Lambda \nabla \times j_s \tag{2.3}$$

$$A = -\Lambda j_s \tag{2.4}$$

Where E is the electric field, B is the magnetic field, A is the vector potential, j_s is the 'super current' density and $\Lambda = m_e/n_s e^2$. In which m_e is the electron mass, n_s is the number of 'super electrons' and e is the electron charge. The second equation can be rewritten to

$$B - \lambda^2 \nabla^2 B = 0 \tag{2.5}$$

Where $\lambda = \sqrt{\Lambda \mu_0}$ is the penetration depth of the magnetic field.

Note that in the two fluid model only the 'super electrons' are responsible for the current in superconductors. The normal electrons do no longer participate in the conduction process once the material has become a superconductor, even if they still form a majority.

[1] Or in groups of two when it is assumed that they form pairs

2.1.3. GINZBURG-LANDAU THEORY

The electrons in a material participating in superconductivity are described by one single wave-function, since superconductivity is believed to be a macroscopic quantum-effect. An increase in ordering in a material can be described using an 'order parameter'.

The Ginzburg-Landau theory[11] considers the wave-function as an order parameter and uses Landau's theory of second-order phase transitions to find the free energy in a superconductor.

This led to the first quantum (phenomenological) theory[2]. At the core of this theory are the Ginzburg-Landau equations:

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m}(-i\hbar\nabla - 2eA)^2\psi = 0 \tag{2.6}$$

$$j_s = -\frac{i\hbar e}{m}(\psi^*\nabla\psi - \psi\nabla\psi^*) - \frac{4e^2}{m}A|\psi|^2 \tag{2.7}$$

Where α and β are parameters that need to be determined experimentally, m is the effective mass, $\hbar$ is the reduced Planck constant, ∇ is the spatial derivative in all dimensions, e is the electron charge, A is the vector potential and i is the imaginary number ($\sqrt{-1}$).

The wave-function and order parameter Ψ of the superconductor is defined as:

$$|\Psi|^2 = n_s \qquad \Psi = \sqrt{n_s}e^{i\varphi} \tag{2.8}$$

Where n_s is the number of superconducting electrons[3] according to the two fluid model and φ is the phase of the superconducting state.

One particularly interesting result that can be derived is the quantization of flux in superconductors:

$$\Phi = n \cdot \Phi_0 \qquad \Phi_0 = \frac{h}{2e} = 2.07 \times 10^{-15} Wb \tag{2.9}$$

Where Φ is the magnetic flux, n is an integer number, Φ_0 is the magnetic flux quantum, h is Planck's constants and e is the electron charge.

The Ginzburg-Landau theory is a phenomenological description: It describes the size of the wave function ξ (also called 'coherence length') and many other useful properties, such as the penetration depth λ and the thermodynamic critical field H_{cm}:

[2] This should not be confused with a 'microscopic theory' such as the BCS theory: the Ginzburg-Landau theory describes the behaviour, but not the origin of the superconducting state

[3] n_s is sometimes used to denote the number of Cooper pairs, which results in an extra factor of two

$$\lambda^2 = \frac{mc^2\beta}{8\pi|\alpha|e^2} \tag{2.10}$$

$$\xi^2 = \frac{\hbar}{4m|\alpha|} \tag{2.11}$$

$$\mu_0 H_{cm} = \frac{\Phi_0}{2\sqrt{2}\pi\lambda\xi} \tag{2.12}$$

2.1.4. BCS THEORY

In 1957 the BCS model[12], named after its founders (Bardeen, Cooper and Schrieffer), proposed that electrons with opposite spin would form pairs, allowing them to occupy the same energy state as other pairs.

BCS theory and other important microscopic theories will be treated in chapter 3.

2.1.5. TYPE II SUPERCONDUCTORS

The early superconductors had no useful applications, because they could only handle very small magnetic fields before losing their superconducting properties. This changed when a new class of superconductors was found.

These type II superconductors let packages of each one magnetic flux quantum (Φ_0) into the material when a first critical magnetic field was reached[13] and only lost superconductivity after a second critical field, which is several orders of magnitude higher.

The behaviour of type II superconductors is described by the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory. The Ginzburg-Landau parameter κ marks the transition between type I and type II superconductors: If $\kappa > 1/\sqrt{2}$, then the the material is a type II superconductor.

The theory also gives an expression for the first critical field H_{c1}, the second critical field H_{c2}, the thermodynamic critical field H_{cm} and the de-pairing current J_d.

$$\kappa = \frac{\lambda}{\xi} \tag{2.13}$$

$$\mu_0 H_{c1} = \frac{\Phi_0}{4\pi\lambda^2} ln\,\kappa \tag{2.14}$$

$$\mu_0 H_{c2} = \frac{\Phi_0}{2\pi\xi^2} \tag{2.15}$$

$$H_{cm} = \sqrt{\frac{H_{c1}H_{c2}}{ln\,\kappa}} \tag{2.16}$$

$$J_d = \frac{4}{3\sqrt{6}}\frac{H_{cm}}{\lambda} \tag{2.17}$$

Where λ is the penetration depth, ξ is the coherence length, μ_0 is the vacuum permeability and Φ_0 is the magnetic flux quantum.

Note that H_{c1} depends mainly on λ, while H_{c2} depends on ξ. The reason for that is simple: H_{c1} is reached when it becomes unfavourable for the field to penetrate further from the side of the material alone, while H_{c2} is reached when flux vortices start to touch each other.

2.1.6. Josephson theory

Having one single wave-function to describe a complete superconductor has some remarkable implications, especially at the junction between two superconductors. This behaviour is related to the phase difference between the wave-functions of the two different superconductors.

The way current flows across these junctions was described by Josephson[14] with the Josephson equations.

$$I = I_c \sin(\Delta\varphi) \tag{2.18}$$

$$V = \frac{\hbar}{e^*} \frac{\partial(\Delta\varphi)}{\partial t} \tag{2.19}$$

Where I is the current with amplitude I_c and phase φ, t is the time, e^* is the charge of the charge carriers, V is the applied potential and $\hbar$ is the reduced Planck constant.

The first equation gives the DC Josephson effect: a constant current without the need for a voltage, but depending on the phase difference between two materials.

The second equation gives the AC Josephson effect: an alternating phase (and with it current) as a result of an applied voltage.

2.1.7. Unconventional superconductors

The BCS theory gives a very accurate description of many superconductors, but it fails for some materials. These materials are called unconventional superconductors.

Most significant is a class of cuprate superconductors with much higher critical temperatures than the earlier superconductors, that was discovered in 1986[15]. These 'high temperature superconductors' have since then become the focus of research. The critical temperatures of up to 150 K (around 100 for practical cuprates) are however still far below room temperature.

More recently a class of iron-based superconductors has been discovered. These materials with critical temperatures up to 55 K are now getting a lot of attention. They include elements from the pnictogen or chalcogen group from the periodic table, and are therefore often referred to as iron-pnictides and iron chalcogenides. Their main interest is academics, since their behaviour is very different from other superconductors, but there are also people who believe that the iron-based superconductors might have practical applications.

At lower temperatures there are also unconventional superconductors. They are either classified as 'heavy fermion' superconductors or 'covalent' superconductors.

2.1.8. Applications

Superconductors might seem like pure academic physics, but they actually already have many applications.

The lack of resistance allows huge currents to flow, without a problematic heat production. Therefore superconducting electromagnets can generate massive magnetic fields. The current in superconductors is accompanied by a phase that can be measured very accurately. This is used for incredibly precise measurements of magnetic fields.

One of the best known devices that depends on superconductors is an MRI scanner. These scanners need huge magnetic fields that can not be generated by conventional magnets in a practical way.

Other applications of superconducting magnets can be found in specialistic fields. One example is the field of high energy physics, which needs particle accelerators, that require massive magnetic fields that have to be generated with superconductors. Another example is nuclear fusion research, where superconducting magnets are required to magnetically confine hot plasmas.

There are also applications for superconductors in electronics. The SQUID (Superconducting Quantum Interference Device) for example is capable of measuring extremely small variations in magnetic fields.

2.2. Real space

In physical terms 'space' simply refers to the dimensions that we are interested in. Mathematically, space refers to the variables we use in the equations; They will appear on the axes of the graph when we plot the function. **Real space** could for example use the spatial variables that correspond to the dimensions height, width and depth(usually denoted with x, y and z). It is also possible to express real space with a different coordinate system, such as spherical coordinates (radius r, horizontal angle θ and vertical angle ϕ).

Different coordinate systems in real space can easily be translated into each other, by using trigonometric functions, such as sine and cosine.

2.2.1. Reciprocal space

Solids are often analysed in **reciprocal space**, where the value of 'wave vectors' is used in stead of the distances. This representation gives useful information when describing something with a wave-character, it matches the data from diffraction measurements and relevant mathematics are often easier than in real space.

The wave vector is usually denoted with the letter 'k' and is proportional to the momentum. For this reason reciprocal space is often also called **k-space** or **momentum space**. The proportionality is given by the De Broglie relation:

$$p = \hbar k \tag{2.20}$$

The wave vector is also related to the wavelength λ.

$$k = \frac{2\pi}{\lambda} \tag{2.21}$$

It is also related to the velocity of the wave, although it should be noted here that a wave has two velocities: The phase velocity is related to the phase change within the wave, while the group velocity is related to the movement of a wave packet as a whole.

It is this group velocity that gives the actual velocity of a particle with a wave-like character. These velocities are given by:

$$v_p = \frac{\omega}{k} \qquad v_g = \frac{\partial \omega}{\partial k} \qquad \omega = 2\pi f \tag{2.22}$$

Where f is the frequency and ω is the angular frequency.

2.2.2. The Fourier transform

Real space and reciprocal space can be 'translated' into each other using a Fourier transform and an inverse Fourier transform:

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(k) e^{ikx} \cdot dk \tag{2.23}$$

$$f(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \cdot dx \tag{2.24}$$

Where $f(x)$ is a distribution in real space and $f(k)$ is its 'conjugate' distribution in k-space. The Fourier transform makes sure that the information is conserved, while it is taken from one space to the other.

The Fourier transform can be applied to many other situations as well. It could for example also transform between frequency and time, which are also 'conjugate variables'.

This has many applications in various fields of science, but that is beyond the scope of this thesis.

2.2.3. Other spaces

Another space that is sometimes used is **phase space**, which shows the 'states' of the system. For a mechanical system this means that the momentum is plotted versus the position, so that all possible combinations of position and momentum (phases) correspond to a point in phase space.

State space is an abstract type of phase space, where coordinates might respond to other types of (often quantized) states. An example of this is a complex **Hilbert space** used in quantum mechanics, where complicated integrals can be calculated with relatively simple vector calculus.

Other variables can also be used, resulting in new spaces. An example is energy, which would give an **energy space**.

3. Microscopic theory

The BCS theory explains many properties of superconductors and it is generally accepted to be a proper description of the microscopic behaviour inside superconductors.

This chapter explains the origin of this influential theory. Assumptions are emphasised, since they will later be used to investigate the limitations of BCS theory.

3.1. The Bohm-Pines collective description

The foundation of BCS theory is formed by the Bohm-Pines collective description [16, 17, 18, 19]. An odd detail is that it was initially derived to describe plasma oscillations in a high density electron gas: It is hard to imagine a state of matter that is further from the superconducting ground state. The description was later extended so that it would apply to metals as well.

It consists of four parts: The first part [16] (BP I) describes the magnetic interaction and is mainly used to illustrate the methods. The second part [17] (BP II) discusses the difference between collective and individual interactions. The third part [18] (BP III) derives the coulomb interaction. The fourth part [19] (P IV) makes the transition to metals.

Bardeen later worked with Pines on an extension of this model that also treats the electron-phonon interaction [20], which is essential to BCS theory.

3.1.1. Approximations

Throughout the derivation several approximations are made. BP I summarizes the most important approximations:

1. Only long range interactions: "The short-range electron-ion and electron-electron collisions are neglected."
2. Linear approximation: quadratic field terms are neglected
3. Random phase approximation (RPA): the phase of surrounding electrons is assumed to be random, so that phase effects average out.
4. Long wavelengths of the density waves.

The RPA is probably the most important assumption in this model.
It is also assumed that the electrons tend to stay apart from each other [20].

3.1.2. Jellium

In order to translate the derived model to solids, it was needed to make an appropriate model of a solid. Pines choose to represent the effect of the positive ions as a smeared out uniform background of positive charge [19]. Conyers Herring gave it the name 'jellium' [21].

Jellium can be thought of as a dense plasma, in which screening plays an important role. Moving electrons will leave a trail of positive charge in jellium, due to the slow response of the heavy positive charge.

There is no real material that actually looks like jellium, but under the right conditions the behaviour of some materials may be comparable to this simplified model.

3.2. BCS Theory

What is now known as the BCS theory is described in a single paper by Bardeen, Cooper and Schrieffer [12]. However, an earlier paper already contained the basic ideas [22].

We will briefly go through the history of the development using the stories as told by Bardeen, Cooper and Schrieffer [23, 24, 25] and by the historian Hoddeson [26].

Bardeen played a central role in bringing together all the knowledge needed to develop this theory. He graduated under Wigner by investigating how electrons inside metals interact. The London theory started his interest in superconductivity, in particular because it was believed to be a macroscopic quantum state. His early attempts to explain this phenomenon failed, just like those of all other scientists who worked on the problem.

After the Second World War Bardeen worked at Bell labs, where he worked under Shockley on the development of the transistor. Bardeen did not like to work under Shockley and so he started working on superconductivity again.

3.2.1. Phonon interaction

The discovery of the isotope effect gave a boost to these attempts, not only for Bardeen but also to his competitor Fröhlich. They both had the idea that the isotope effect could be explained if lattice vibrations where responsible for superconductivity.

Bardeen eventually left Bell labs and started to work on superconductivity only. He learned about the work of Pines, who he offered a postdoctoral position. Together they modified the Bohm-Pines theory to include the phonon interactions, which led to the finding of an attractive electron-electron interaction.

3.2.2. Pairs

Bardeen then looked for new students to help him with his search for a theory on superconductivity. This search led him to Cooper and Schrieffer.

In 1955 Cooper had a breakthrough : He found that electrons can form 'Cooper pairs' [27] with an attractive force between them, through virtual phonons. He also noticed that there was an energy gap between the superconducting state and the normal state.

3.2.3. Wave-function

In 1956 Bardeen won the Nobel prize for his work on the transistor. At this time Schrieffer thought about leaving the team, but Bardeen convinced him to stay a bit longer.

Schrieffer listened to Bardeens advice and not much later he came up a wave-function that worked for the Cooper pairs.

3.2.4. Energy gap

With this wave-function they managed to derive the energy gap and within weeks they published the first paper on their theory [22].

After that they worked on extending and improving their theory, which eventually led to their famous article [12]. Here they derive equations for many important properties of superconductors. Most important are the band gap Δ_0, the critical field at absolute zero $H_{cm}(0)$, the density of states $\rho(E)$, the coherence length ξ_0 and the critical temperature T_c:

$$\Delta_0 \simeq 2\hbar\omega_D \, e^{-1/N(0)V} \tag{3.1}$$

$$H_{cm}(0) = \Delta_0 \sqrt{4\pi N(0)} \tag{3.2}$$

$$\rho(E) = N(0) \frac{E}{\sqrt{E^2 - \Delta_0^2}} \tag{3.3}$$

$$\xi_0 = 0.18 \frac{\hbar v_F}{k_B T_c} \tag{3.4}$$

$$T_c = \frac{2\Delta_0}{3.52 k_B} \tag{3.5}$$

Where $\hbar$ is the reduced Planck constant, ω_D is the Debye frequency, $N(0)$ is the density of states at the Fermi level, V is the attractive potential, E is the energy and $v_F = k_F / m_e$ is the Fermi velocity.

The derivation of these equations can be found in appendix A.3.

3.2.5. Mathematical tools

It should be noted that the BCS equations did not simply turn up at the moment when the pairing mechanism was proposed. This required some very specific mathematical tools:

First of all a significant part of the derivation of the BCS equations was formulated in the mathematical 'language' of **second quantization**. In this formalism quantum mechanical states are evaluated one by one, by creation and annihilation.

This is done by applying the creation operator $\hat{c}^\dagger$ and the annihilation operator $\hat{c}$ to states with wave vector k. The sum is then taken over all relevant states. The BCS model Hamiltonian can be expressed in this language, which looks like

$$H^{BCS} = \sum_{k,\sigma} \hat{c}^\dagger_{k\sigma}(\epsilon - \mu)\hat{c}_{k\sigma} - V \sum_{k,k'} \hat{c}^\dagger_{k'\uparrow}\hat{c}^\dagger_{-k'\downarrow}\hat{c}_{-k'\downarrow}\hat{c}_{k'\uparrow} \tag{3.6}$$

Another commonly used tool is **perturbation**, which is a Taylor series around a relevant point (such as the critical temperature).

Finally, the **Hartree-Fock** method is used to accurately approximate many particle systems. This is done by summing over the effect of the many involved particles in a clever way.

3.3. The law of phonon mediated interaction

The road to BCS presented in this chapter is the historical road that was taken. A closer look at the derivation of the BCS equations reveals that not all elements are equally important.

The complete set of BCS equations can be derived from one simple assumption: The law of phonon mediated interaction, which states that *electrons with energies that differ from the Fermi energy by no more than $\hbar\omega_D$ are attracted to each other*[3].

The pairing mechanism gives this law in a natural way, since only such an indirect interaction can cause equally charged particles to attract each other. However, other mechanisms could form an equally suitable basis for the BCS equations, as long as they lead to phonon mediated interaction.

The phonon mediated interaction does for example not restrict the amount of interactions per electron to only one.

It has even been argued that the attractive interaction could have a different origin is some cases[28], so that even the phonons might not always play an essential role in superconductivity.

The overall development of the BCS theory, including the phonon mediated interaction, has been summarized in figure 3.1. The Bogolyubov equations and some of the important results that follow from it are discussed in the next section.

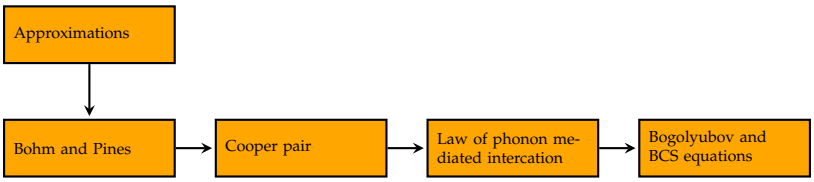


Figure 3.1.: Development of the BCS theory

3.4. The self-consistent field method

The BCS theory did not stay unnoticed in the Soviet Union, where scientists quickly began to improve and extend this new theory [29].

3.4.1. Bogolyubov equations

A significant extension has been made by Bogolyubov: The Bogolyubov equations generalize the BCS theory and make it applicable to non-homogeneous materials. These equations give an expression for a coupled system and contain a spatial dependence:

$$\epsilon u(r) = \left[\mathcal{H}_e + U(r)\right] u(r) + \Delta(r) v(r) \tag{3.7}$$

$$\epsilon v(r) = -\left[\mathcal{H}_e^* + U(r)\right] v(r) + \Delta^*(r) u(r) \tag{3.8}$$

Where $u(r)$ and $v(r)$ are the wave-functions of the system and ϵ corresponds to the eigenvalues. The essence can be represented as the eigenvalue problem:

$$\epsilon \begin{pmatrix} u \\ v \end{pmatrix} = \hat{\Omega} \begin{pmatrix} u \\ v \end{pmatrix}$$

With eigenfunctions $\binom{u_n}{v_n}$ and eigenvalues ϵ_n.
The operator $\mathcal{H}_e$ and the potentials U and Δ are given by:

$$\mathcal{H}_e = \frac{1}{2m}\left(-i\hbar\nabla - \frac{eA}{c}\right)^2 + U_0(r) - E_F \tag{3.9}$$

$$U(r) = -V \sum_n \left[|u_n(r)|^2 f_n + |v_n(r)|^2 (1 - f_n) \right] \tag{3.10}$$

$$\Delta(r) = +V \sum_n v_n^*(r) u_n(r) (1 - 2 f_n) \tag{3.11}$$

Where m is the mass, $\hbar$ is the reduced Planck constant, e is the electron charge, A is the vector potential, c is the speed of light, E_F is the Fermi energy and f_n is the occupation number given by:

$$f_n = \frac{1}{e^{\beta \epsilon_n} + 1} \tag{3.12}$$

Where ε_n is the energy of state n and $\beta = 1/k_B T$ with Boltzmann constant k_B and temperature T. $(1 - f_n)$ is then of course the probability of having an unoccupied state.

The potentials U and Δ are also known as the self-consistency equations. U is called the Hartree-Fock potential and comes from a sum involving all states below the Fermi level. It can often be approximated with the Hartree-Fock potential in the normal state. In homogeneous materials the pair potential Δ simplifies to the uniform energy gap. In contrast to U it is strongly dependent on the temperature.

3.4.2. Correlation function

In non uniform materials equation 3.11 no longer represents a gap, but this potential does have significance. This becomes clearer as we investigate the variation of this potential over the material.

Therefore we will consider a different coordinate s and investigate its dependence on the potential of its surrounding, by integrating over all positions r:

$$\Delta(s) = \int K(s,r)\Delta(r)dr \tag{3.13}$$

And in the presence of magnetic fields:

$$\Delta(s) = \int K_0(s,r)e^{-[2ieA\cdot(s-r)]/\hbar c}\Delta(r)dr \tag{3.14}$$

Where K is called the kernel (K_0 is the kernel at the critical temperature).

This kernel represents the correlation between the two potentials. It can be shown [5] that for a pure metal the kernel scales with the coherence length ξ_0. However for a 'dirty metal', where the distance l between impurities is much smaller than ξ_0, the kernel scales with $\sqrt{\xi_0 l}$.

The exact results are given below:

$$\frac{K_0(R)}{N(0)V} = \frac{k_B T_0}{2\hbar v_F}\frac{1}{R^2}e^{-1.13R/\xi_0} \qquad (R << l) \tag{3.15}$$

$$\frac{K_0(R)}{N(0)V} = \frac{k_B T_0}{\hbar D R}e^{-1.8R/\sqrt{\xi_0 l}} \qquad (R >> l) \tag{3.16}$$

Where $R = s - r$, $N(0)$ is the density of states at the Fermi level, V is the attractive potential, k_B is the Boltzmann constant, T_0 is the critical temperature, $\hbar$ is the reduced Planck constant, v_F is the Fermi velocity and $D = v_F l/3$ is the diffusion coefficient.

Further calculation gives the Ginzburg-Landau equations, for both pure and dirty metals.

4. BCS IN REAL SPACE

4.1. QUASI-PARTICLES AND VIRTUAL PHONONS

It is possible to collect the abstract concepts often used to describe BCS theory and to summarize the theory as 'quasi-particles exchanging virtual phonons in reciprocal space', as was already mentioned in the introduction. In this section the meaning of this phrase will be explained.

4.1.1. QUASI PARTICLES

Particle excitations in superconductors generally do not behave like excited electrons. Sometimes they even behave like holes (a 'missing electron', corresponding to a charge of +1).

This can be understood by looking at the screening mechanism: Single particle excitations are unlikely in solid: in general there are other particles that respond. This means for example that the negative charge of an electron will attract the positive ions, which will ideally cancel the electron-charge. If the electron moves, the ions will not be able to perfectly match its behaviour, so that the electron will be under-screened or over-screened. In the extreme case the electron will already have left, when a matching screening-charge arrives, leaving a +1 charge.

The charge of a quasi particle is related to its wave-vector:

$$q_k = \frac{\varepsilon_k}{\sqrt{\varepsilon_k^2 + \Delta^2}} \tag{4.1}$$

Where ε_k is the energy corresponding to the wave-vector k and Δ is the energy gap.

It is good to remember that the only fundamental particles involved are quarks, electrons and photons. Everything else is eventually just a combination of these particles, or a manifestation of their behaviour. Sometimes it is convenient to treat specific combinations (usually ones that are quantized) as particles, but this is nothing more than a convenient model.

4.1.2. PHONONS

Particles and waves are closely related. It is now known that every particle can be described as the manifestation of a corresponding field of waves. A simple example of such duality is the photon, which is the particle that correspond to light waves.

It becomes slightly less clear when you start assigning non-fundamental particles to various types of waves in materials. Phonons are vibrations of the atomic lattice and can be considered as excitations of an elastic field. An overview of important excitations in solids is given in table 4.1

Particle	**Field**
Electron	—
Photon	Electromagnetic wave
Phonon	Elastic wave
Plasmon	Collective electron wave
Magnon	Magnetization wave
Polaron	Electron + elastic deformation
Exciton	Polarization wave

Table 4.1.: Important excitations (Table taken from [30, p.90])

The phonons have many properties that are also associated with fundamental particles. Some of the most remarkable are the quantization of energy and the presence of zero-point energy. There is also a momentum associated with phonons. This 'crystal momentum' is defined according to the De Broglie relation (see chapter 2), but there is no moving mass such as with a real momentum.

4.1.3. VIRTUAL PARTICLES

In high energy physics virtual particles are energy fluctuations that have all the characteristics of an elementary particle, but do not necessarily have the right mass. One effect is that their energy and momentum are not always conserved, which is in high contrast with real particles. They are also far less stable than the real particles, which means that they generally decay much faster.

They are often responsible for interaction between real particles. Charged particles for example interact by exchanging virtual photons and it is believed that particles get mass by generating and reabsorbing virtual Higgs bosons (a form of self-interaction).

4.1.4. 'Quasi-particles exchanging virtual phonons in reciprocal space'

Now let us now investigate the virtual phonons that are exchanged between our quasi-particles: The quasi-particles themselves would be screened electrons; The phonons are lattice vibration and the fact that they are virtual means in this case that they only exist for a short time.

Their short existence starts when an electron moves through the lattice and distorts it. This distortion turns into a vibration (the phonon) when the electron has passed. A second electron could take the energy out of this vibration, when it is attracted by the extra positive charge.

The analysis is usually carried out in reciprocal space, but this does not change any of the physical behaviour discussed above.

The most simple visualization of this phonon mediated interaction is figure 1.1. The presence of a phonon mediated interaction however does not directly mean that there is a bound state.

4.2. Movement

The presence of an attractive interaction requires a circular movement: The attractive force gives an acceleration towards the center of mass, which would eventually result in a collision, unless there is a movement perpendicular to this acceleration. Movement away from the center of mass would effectively cause the pair to break up over time.

A true bound state [27] with a constant radius can also only be possible if there is no movement towards or away from the center of mass. This again means that there can only be movement in the angular direction.

This circular type of movement is schematically represented in figure 4.1.

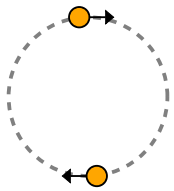


Figure 4.1.: Electrons circling each other

In order for electrons to feel the full extent of each others potential wake, they must meet each other head-on[31]. They will then start to follow each others wake and form a bound state.

This bound state would be very similar to that of for example positronium: a bound state between an electron and its anti-particle, the positron.

4.2.1. JELLIUM IN REAL SPACE

It should be noted that this model still contains some important assumptions, that have been made in deriving the BCS model. The most significant is probably the use of the jellium model.

It might be informative to investigate how this substance responds to moving electrons.

Jellium, as mentioned earlier is a model where electrons move through a uniform positive background charge. The screening effect is in practice described by a dielectric constant $\epsilon(q, \omega)$ that depends on the wave vector q and the freqency ω.

$$\frac{1}{\epsilon(q,\omega)} = \frac{q^2}{K_S^2 + q^2}\left[1 + \frac{\omega_q^2}{\omega_i^2 - \omega_q^2}\right] \tag{4.2}$$

Where the width of the phonon spectrum ω_i, the plasma frequency ω_p, the phonon frequency ω_q and the Fermi-Thomas wave vector K_S are given by

$$\omega_i = \sqrt{\frac{4\pi n Z e^2}{M}} \sim \omega_p \sqrt{\frac{M}{m}} \qquad \omega_p = \sqrt{\frac{4\pi n e^2}{m}} \qquad \omega_q = \sqrt{\omega_i^2 \frac{q^2}{K_S^2 + q^2}} \tag{4.3}$$

$$K_S^2 = \frac{6\pi n e^2}{E_F} \tag{4.4}$$

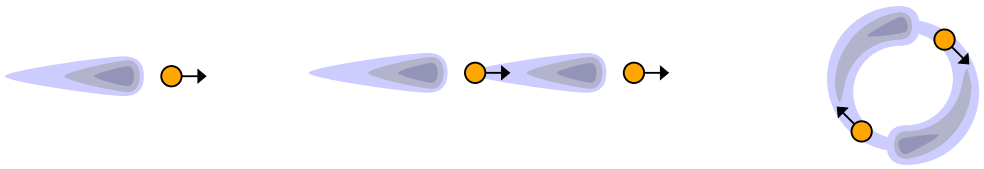
Where n is the electron density, e is the electron charge, E_F is the Fermi energy, M is the ion mass, m is the electron mass and Z is the valence of the metal.

For an average phonon $\omega_q \sim \omega_D$, where ω_D is the Debye frequency[5]. Note that the mass dependence of the frequencies gives the isotope effect.

The screening length is the Debye length λ_D, which is the inverse of the Fermi-Thomas wave vector K_S^2.

$$\lambda_D = \frac{1}{K_S} = \sqrt{\frac{E_F}{6\pi n e^2}} \tag{4.5}$$

To illustrate what this means in practice, the following schematic pictures of charge density were created by the author of this thesis: Figure 4.2a shows how an electron (dark spot) leaves a trail of positive charge. Figure 4.2b shows a second electron following this trail. Figure 4.2c shows the behaviour that is also represented in figure 4.1, where two electrons follow each other on a circular path.



(a) One electron (b) Two electrons (c) Circular

Figure 4.2.: Example pictures for jellium

This last picture is particularly informative, since it visualizes both the phonon mediated interaction and the relative movement of the electrons. No similar pictures have been found in literature, which suggests that this is the first time that the Cooper pair is visualized in this way.

4.2.2. The pair function

A more exact analysis was done by Kadin [1]. He used the pair function (also known as singlet pair function or Gor'kov F function[32]) to calculate the real spatial structure of a Cooper pair. Kadin showed that

$$\Psi(r) \propto \sum_k u_k v_k e^{ikr} \propto \cos(k_F r) K_0(r/\pi\xi_0) \tag{4.6}$$

$$\rho(r) \propto [1 + \cos(2k_F r)] e^{(-2r/\pi\xi_0)/r} \tag{4.7}$$

Where Ψ is the wave function, ρ is the charge density, u and v are states, k is the corresponding wave vector, r is the radius, ξ_0 is the coherence length and K_0 is the zeroth-order modified Bessel function which looks somewhat similar to an exponential decay. The result was an onion-like layered structure, plotted in two dimensions in figure 4.3. In real space this would be three dimensional.

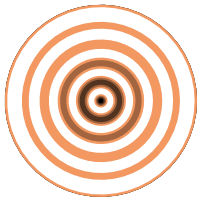


Figure 4.3.: S-wave, based on Kadin's calculations[1]

The total size is proportional to ξ_0, due to the natural exponential function. The variations happen on a smaller scale, proportional to the k_F in the cosine. This figure represents not only the charge modulation of the electrons, but also of the underlying positive charge. Many of these pairs would overlap and form a 'solid' structure of pairs, that would move as a whole when transporting electricity. All of these pairs would have to be in phase, in order for the macroscopic phase coherence to exist.

The s-wave symmetry corresponds to the low temperature superconductors. Other symmetries might apply to different type of superconductors, but these will not be discussed here. Also, it is only valid in the clean limit, where the size is directly proportional to ξ_0: In the dirty limit it will be smaller, since there the size is proportional to $\sqrt{\xi_0 l}$.

This structure can be seen as a Fourier transform of the ground state distribution in reciprocal space[33].

4.2.3. Exclusiveness

The visualizations presented here all follow directly from the BCS theory. Not only the S-wave in figure 4.3, but also the schematic figures 4.1 and 4.2c form a proper basis for the BCS equations, due to phonon mediated interaction.

These figures were obtained by eliminating the possibilities for relative movement within the BCS model. This means that the visualizations are not only correct[1], but also exclusive, in the sense that if Cooper pairs exist in the way predicted by BCS theory, then they must look like this.

This is important since it allows us to examine the BCS model through this real space behaviour.

[1] Although in some cases schematic

5. Alternative model

It is believed that Lev Landau once said that there is an infinite number of wrong theories, that can all explain one correct observation.

The only way to be certain that a theory is correct, is probably to eliminate all other theories. Therefore, to see whether BCS theory is correct, we will investigate whether a different theory could give a proper explanation of superconductivity. Such an alternative will not disprove BCS theory, but it will question its validity, which is often taken for granted.

It has become clear by now that the BCS equations give a correct description of many of the properties of conventional superconductors. But on the other hand it has also become clear that these equations fail when it comes to explaining other classes of superconductors, including the high temperature cuprates.

An often proposed explanation is that these other classes of superconductors have a fundamentally different origin of their superconductivity. Another explanation might be that the BCS equations are incomplete or even incorrect. However, this explanation is less popular, since it seems to imply that the entire BCS theory, including its successful equations, is wrong.

In chapter 3 it was noted that the only thing required for the BCS equations is an attractive force, for example due to a phonon mediated interaction. Such an interaction does not strictly need the Cooper pairs: The interaction can be between multiple electrons and its strength even change over time. The Cooper pairs then become just a qualitative explanation for the macroscopic coherence, that is no longer a requirement for the equations.

This means that the successful BCS equations can remain untouched by an alternative model, as long as it accounts for an attractive force between electrons.

This chapter discusses possible alternatives to the BCS theory, that still lead to the BCS equations. First a model proposed by Kadin[33] is discussed. Later on the third law of thermodynamics is used to derive the behaviour of electrons in a material near absolute zero. This leads to the same model that Kadin derived from charge density waves.

5.1. Superconductivity without pairing

This section discusses a model that has been proposed by Kadin[33]. It is closely related to an early model proposed by Fröhlich, which suggests that superconductivity might be a result of charge density waves (CDW).

Kadin points out that the phase transition and energy gap of CDW are described by the exact same equations as the BCS energy gap and that both phenomena are based on the same electron-phonon interaction.

It is commonly believed that CDW pin to defects turning the material into an insulator, but the high frequency (THz) may prevent this from happening.

In stead of a full transition to the CDW state the material might also show related behaviour on a smaller scale, when so called Kohn Anomalies form.

The standing CDW would form a 'virtual phonon lattice' which would force the electrons to form a crystal structure, with alternating phases. These alternating phases will cause neighbouring electrons to have a 180 degrees phase difference and a node between them. This would allow them to form a repeating phase pattern without violating the Pauli exclusion principle. In this way the material will still show macroscopic coherence.

The two phase ordering also gives a factor of 2e in the flux quantization, which is usually attributed to be the result of pair forming.

The ordering would have a similar effect in super-fluids, such as He-4.

Kadin also indicates that other mechanisms, such as spin density waves might give similar results. These might be responsible for the superconductivity in some of the unconventional superconductors.

5.2. Derivation

Here we will derive an alternative to the BCS model, which will be analysed and compared.

Bohm and Pines started with a model for a plasma: a chaotic system with a lot of energy. It was then modified until it was believed to be valid for metals at absolute zero. Here we will take an almost opposite approach, by starting at absolute zero.

The starting-point for this model is to assume that superconductivity does not only exist close to absolute zero, but also at absolute zero. This way we can use the **third law of thermodynamics**: At absolute zero a system should settle in its unique lowest energy state[34]. There are exceptions, where residual entropy remains. These will be discussed later on, but at this moment we will assume a unique ground-state.

This uniqueness of the ground-state significantly simplifies the derivation: The ordering should be maximum, so that no randomness remains. This prevents random movements from adding up to a scattering event. It is therefore clear of any resistance, which makes it a reasonable basis for the ground state of superconductors.

The only variations still allowed, are standing waves related to the zero-point energy.

The next step is to start with a simple classical model of a solid made out of particles. This will gradually be extended to a full quantum-mechanical system.

From a classical point of view there is no kinetic energy at 0K. The band structure of metals however still gives some free electrons.
All these 'free' electrons must have fixed positions, determined by the potential energy landscape. The ions in the crystal give a fixed periodic potential, which will arrange the electrons in a fixed grid, in a shape related to the ion grid.
Such a solid structure out of electrons is known to be possible outside a solid, where it is known as a **Wigner crystal**.

A big difference between classical physics and quantum physics at 0K is the presence of **zero point energy**. So to improve this model, it is necessary to add some kinetic energy.
First we will add a little bit of energy to one of the electrons and keep everything else at fixed positions. This will result in an (harmonic) oscillation around its original equilibrium position.
The next step is to allow the other electrons and the ions to move as well. There is still no external force, so the centres of mass must be stable. This means that the movement of every electron needs to be compensated by the movement of other particles. Compensation by neighbouring electrons would be most symmetric and therefore probably most stable. Neighbours with opposite spin would be preferred due to Pauli's principle.
Now electrons will oscillate in the opposite direction of their neighbours, while the ions only oscillate in directions perpendicular to this movement. This is represented in figure 5.1, where the gray dots represent the ions.

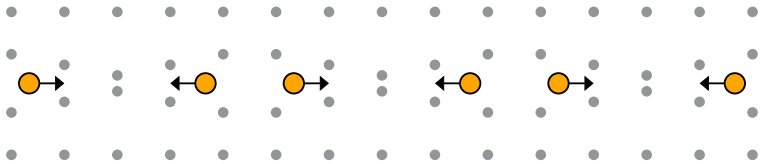


Figure 5.1.: Alternative model for electron movement

The oscillation gives the electron a linear trajectory, which is the simplest trajectory for an electron. Other trajectories, such as the circular one proposed in chapter 4, would reduce the ordering, which could lead to scattering events.
Extending this picture would lead to a 'solid structure' of oscillating conduction electrons, that exists within the ion grid. From a quantum-mechanical point of view there will be just a localized standing wave.
Once this transition has taken place, the order can only be further increased through phase coherence.

5.3. PHASE AND SUPERCONDUCTIVITY

The important role of phase in superconductivity has been known for quite a while now: The electrons in the ground state are known to be phase coherent, so that their wave functions add up. The wave function and order parameter of the superconductor (also given in chapter 2) can be written as:

$$|\Psi|^2 = n_s \qquad \Psi = \sqrt{n_s}e^{i\varphi} \tag{5.1}$$

Where n_s is the number of superconducting electrons[1] according to the two fluid model and φ is the phase of the superconducting state.

This wave-function forms the basis of both Ginzburg-Landau theory (by Taylor expanding it around the critical temperature) and the Josephson equations (by solving the Schrödinger equation for a coupled system).

5.3.1. AN ALTERNATIVE TO THE TWO FLUID MODEL

It is clear that the two fluid model is not an accurate description of the alternative model: Not only are the electrons in the alternative model not a fluid, but also there seems to be no reason for them to switch from random phase to complete coherence instantaneously one by one.

Here we will demonstrate that the two fluid model might still apply, when we use a different model. This model assumes a gradual increase in correlation between the phases of all the involved electrons. The foundation of this model is the standard result for interference, which is derived in appendix A.5:

$$\rho = n + n\cos(\Delta\varphi) \tag{5.2}$$

Where ρ is the density of the electron wave-function, n is the number of real electrons involved and $\Delta\varphi$ is the average difference between the phase of electrons.

Note that φ has a maximum value of 2π, but that $\Delta\varphi$ has a maximum value of π. The reason is that due to the periodicity of φ any difference between φ_1 and φ_2 of $|\pi + x|$ can also be expressed as $|x - \pi|$. The absolute value was taken because a properly defined phase difference will not be negative.

Therefore a random (equal) distribution of phase among the electrons will give an average $\Delta\varphi$ of $\pi/2$ and therefore $\rho = n$.

The total amount of charge does not seem to change in superconductors, which means that on average over the material there is not one single phase. However, on a local scale there might still be phase coherence, as is also predicted by the alternative model. Some form of phase coherence of the superconducting state is also generally assumed.

[1] n_s is sometimes used to denote the number of Cooper pairs, which results in an extra factor of two

A structure of alternating phases would have an equal amount of constructive and destructive interference, so that the effective electron density over the complete material is the same as for the normal case. There is however a difference in ordering and interference does occur on a local scale. The degree to which an electron contributes to this ordering is determined by the degree of coherence (correlation when averaged over the material) with its second neighbour $\cos(\Delta\varphi)$. This correlation can also be expressed in coherence with its direct neighbour, which ideally has a phase difference of pi, so that the coherence is related to $-\cos(\Delta\varphi)$. This can be directly translated to the superconducting electrons in the two fluid model:

$$n_s = -n\cos(\Delta\varphi) \tag{5.3}$$

Where n_s is the number of superconducting electrons according to the two fluid model[2], n is the number of real electrons involved and $\Delta\varphi$ is the average difference between the phase of electrons and that of their direct neighbours.

This means that all electrons contribute to the superconducting wave-function, but to a degree that is determined by the correlation between their own phase and that of their direct neighbour.

This new model does not require electrons to suddenly switch between two fluid phases (from random to completely correlated)[3] it only involves a certain degree of phase coherence between neighbouring electrons. Therefore it is applicable to both the BCS model and the alternative model.

This mechanism of interference also shows a weakness in the two fluid model: Every electron contributes to to the superconducting phase (either trough constructive or destructive interference), unless it is exactly 90 degrees out of phase with its direct neighbours. If that was the case for all normal electrons, then they would be phase coherent and therefore presumably superconducting. This would also be impossible because of the exclusion principle, which still applies to normal electrons.

The normal phase therefore has to be random, so that phase coherence is exclusive to the superconducting phase. The coherence would not increase electron by electron, but on average all electrons phases would become correlated as the temperature drops from the critical temperature to absolute zero. All electrons would therefore be 'super electrons' to some degree.

The constructive and destructive interference would cause large differences in charge density from the electrons on the scale of individual electrons, that depend only on the phase of these electrons. Disturbances in phase will therefore change the local charge distribution, without physically moving electrons.

[2]The number of Cooper pairs would be half this number

[3]although it would still apply in that case

5.3.2. Pauli's principle

According to the Pauli exclusion principle identical fermions (such as electrons) can usually not occupy the same state. There is however an exception, for fermions that are exactly 180 degrees out of phase, with a node between them [33].

Another way around this principle is to have bosons, which is the argument generally given for Cooper pairs. The Cooper pairs however are not bosons[22, 12], but they are still considered to be sufficiently 'boson-like' to obey the same ground state.

In the alternative model one could pick two arbitrary neighbouring electrons and call them a pair. Each electron is a standing wave that exists between two nodes and the two are exactly 180 degrees out of phase. Therefore it seems to be a full wavelength of the electron wave-function. The charge would be $2e$ and the spin would be zero, due to the opposite spin of these neighbours.

One could argue that every such full wavelength is a boson. This might even make more sense than calling two distant electrons a boson, just because they interact.

Finally, it is also possible that the electrons are not in their ground state, but that an ordered distribution of their different phases still causes macroscopic quantum effects. It might for example be possible that the phase difference between an electron and its second neighbour would not be 0, as in the ideal case, but $\delta\varphi$, which is the minimum difference between the two phases allowed by the exclusion principle.

The phase would then gradually change over the length of the material.

5.3.3. The effective potential

The Josephson equations (also given in chapter 2) state that the current depends on a phase difference and no longer directly on the voltage:

$$I = I_c \sin(\Delta\varphi) \tag{5.4}$$

$$\frac{\partial(\Delta\varphi)}{\partial t} = \frac{e^* V}{\hbar} \tag{5.5}$$

In resistive materials the current would have depended on the voltage U and the resistance R, in agreement with Ohms law:

$$I = U/R \tag{5.6}$$

This means that the phase difference has effectively taken the role of the potential and is now creating a tendency to accept electrons into the material, or throw them out.

This 'effective potential' from a phase gradient would be negligible for a random phase distribution and it would only become notable with a large phase coherence.

The lowest energy state of the system is one of maximal phase coherence. Any disturbance, such as the addition of an electron pair with a different phase, will be transported

through the material in the form of a phase shift. The system can gain energy by getting rid of this additional phase shift, which can be done by throwing out an electron pair somewhere else. Note that throwing out just one electron will only increase the disorder.

The discussion on the role of phase has not yet clarified how charge can be transported lossless. Actually it is not even clear why this material should conduct at all.

To give a possible explanation we will formulate the hypothesis that superconducting materials have a ground-state which has a multiplicity that is larger than one. This means that there are several electron distributions possible, that are equally stable. It should not be hard to imagine that no energy can be lost in switching between these ground states. Which ground state is most stable depends on the phase distribution. Therefore a phase shift in such a system would be accompanied by the movement of charge.

Another explanation may be derived from the interference: Destructive interference may allow electrons to be transported without acting as charge carriers, or constructive interference may cause electrons to act as multiple charges, without requiring the energy to transport the extra charge.

6. Discussion

In this chapter we will discuss the two different models. We will first look at the implications of the BCS model in real space. Later we will look into the validity of the alternative model.

This chapter ends by proposing methods to further clarify the validity of both models: Experiments are proposed, just as a method to make the alternative model more quantitative.

6.1. Limitations of BCS

Let us now start by looking at the BCS model. Our real space representation of the pairing interaction might give us peculiar behaviour that could follow from superconductivity according to the BCS model.

6.1.1. Behaviour of the real-space Cooper pair

The visualization represented in chapter 4 fixes the main issues within Anderson's representation: The electrons now move in opposite direction and an attractive force is constantly acting upon them. This visualization also does not require the pair to move, as was the case in Anderson's representation.

This, in combination with its simplicity makes it a powerful tool to understand the pairing mechanism according to the BCS model.

The relation of this visualization to the BCS theory is shown in figure 6.1.

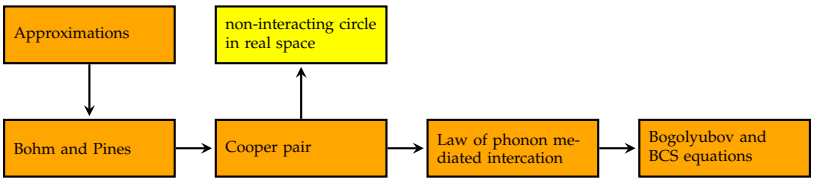


Figure 6.1.: Relation between visualization and BCS theory

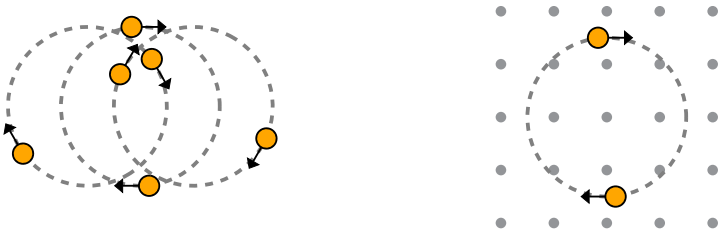
Now that we know what Cooper pairs look like, it is time to investigate whether they exist.

The exclusiveness derived in chapter 4 means that the physical validity of this representation directly reflects the physical validity of the BCS model. This offers a great opportunity to take a critical look at the BCS model.

The first property that can be noticed, especially in the s-wave symmetry, is that there are two equal charges occupying the same position, rather than repelling each other. In addition there should also be a matching positive charge from ions at this same position, in order to keep the electrons in place, so that there is a total amount of four particles at the exact same position.

Another interesting property that can be noticed, is that the particles move on a circular path. This path not only goes straight through other electron pairs, but also crosses the ion grid, which does not have this circular shape, as is illustrated in figure 6.2.

In classical mechanics this would be impossible, but in quantum mechanics this might actually be happening. However it should be noted that here, it is not a result derived from quantum mechanics, but a consequence of assumptions made to simplify the mathematics: The interactions between pairs and between electrons and ions are simply ruled out by the assumptions in the model.



(a) Other pairs (b) Ion grid

Figure 6.2.: No collisions?

One could ask whether it is a problem that collisions are not allowed: maybe they would not happen anyway, or maybe they do without changing anything. Electron-electron scattering for example does not cost electric energy, since it is only redistributed.

6.1.2. The assumptions

The reason for this odd behaviour becomes clear when we look at the assumptions on which the BCS model is based. The most obvious assumptions are:

- Random Phase Approximation (RPA)
- Jellium model
- Point-like interactions

These assumptions were made to simplify the mathematics, but a close analysis might give the impression that they were carefully selected in order to allow the BCS pairing mechanism[1].

[1] There are no indications that such a thing was done on purpose

The RPA prevents order in the phase distribution. The validity is questionable, since in superconductors phase is directly related to the current. The phase is not random and phase differences can even be calculated with the Josephson equations.

The jellium-model by definition ignores the lattice structure. It also prevents interactions with ions and allows arbitrarily high charge densities. It is only valid if all variations in the material are on a scale that is much smaller than variations in the electron wave-function. This means first of all that the materials should be isotropic. Secondly, the electron wave-function and its variations should be large compared to the inter-atomic spacing.

This last requirement seems to be in conflict with the point-like interaction which is generally assumed in BCS theory[5]. Point-like interactions are also a far-reaching assumption when a large overlap between electrons is assumed.

All these limiting assumptions prevent particles from cooperating in order to reach the minimum energy of the ground state.

One could also ask the question: "Why would electrons be restricted to interact with only one other electron?"

To summarize: the peculiar behaviour of electrons, described at the beginning of this chapter, does not form a problem within the assumptions of the BCS model, but this counter-intuitive behaviour does raise the question whether all the assumptions made in the BCS model are strictly valid in all real materials.

6.1.3. Doubts about BCS

This raises the question whether the BCS model really is the right model. The impressive agreement between BCS theory and experiments, still seems to suggest that it is. This is however no guarantee, because sometimes poor models give good results. An example is the free electron model, about which Pines states: "It is rather puzzling that such an independent electron model should have been so successful qualitatively, and in many cases quantitatively..." [19]

It should also be noted, that the assumptions are not explicitly used to derive the BCS equations. This derivation only assumes that electrons close to the Fermi surface might interact, as long as the sum of their wave vectors does not change. This could also have been derived from the conservation of momentum and notion that the interaction energy near absolute zero is limited.

The requirements suggested by BCS theory say very little about whether a material is actually a superconductor, since "We have not found any indication so far that a material having all these properties is a superconductor."[3, p. 160]

Questions have already been raised about the validity of BCS theory [35] and alternative models have been suggested [33].

It appears that although the BCS equations are correct, the underlying model might have some limitations in its capability in describing the actual interactions.

To clarify the validity of the BCS model, we will now investigate whether an alternative model might be able to properly describe superconductivity, without making far-reaching assumptions, such as those described in this chapter.

6.2. THE ALTERNATIVE MODEL

The alternative model derived in chapter 5 has to be compatible with all existing knowledge about superconductors. It has already been shown that the following results are compatible:

- BCS equations (phonon mediated interaction)
- Two fluid model (correlation of wave-functions)
- All in the ground state (out of phase neighbours)
- Double charges (two-phase ordering)

An electron pair with opposite spin and momentum also looks very similar to the Cooper pair described by BCS theory, but there are parts of the BCS model that require a major re-interpretation:

- Electrons interact with all their direct neighbours and one could even argue that the electrons that are an even amount of positions from their direct neighbours are also 'partners'.
- The two fluid model only makes sense as a model, since correlation is increased gradually.
- Treating electrons as point particles might still work for a schematic representation, but to analyse their behaviour it is probably required to take the distribution of the standing wave into account.
- The coherence length represents the size of just one electron. It was actually derived as such in the BCS theory, but the proposed bound state leads to the interpretation as the size of a pair.
- The effect of screening is very modest due to the symmetrical behaviour: electrons move straight at each other leading to interactions, no matter how dense the positive charge.
- The phonon coupling is no longer essential for an 'attractive force': It will however still be relevant, since it is favourable for the electrons to move in phase with the lattice whenever the electron frequency is below the Debye frequency.

The electrons in this model oscillate around relatively fixed positions due to the potential, which is similar to Mott-insulators, making low temperature superconductors look like high temperature superconductors.

It is clear that this coherent 'super crystal' is a macroscopic quantum effect. Maybe even clearer than in the case of randomly moving bosonic electron pairs. Furthermore this ordered crystal structure clearly has a lower entropy than a system where electrons form pairs, but are not further restricted in their behaviour.

According to this model the potential landscape determines the electron behaviour, which in turn results in a phonon interaction at low temperatures. This mechanism would be asymmetric for holes and electrons, since the potential landscape from the atoms and ions is asymmetric around zero potential.

The strong dependence on the potential landscape is not expected to give spectacular results for isotropic materials, but superconducting materials with large internal differences in electro-negativity are expected to behave quite different from the general BCS theory. Also small coherence lengths (compared to atomic spacing) would result in behaviour that deviates from general theory.

This picture implies a phase transition between a liquid and a 'solid' phase for electrons inside the material. Electron crystals have been observed in various superconductors and in Iron Pnictides it seems likely that they play a key role in the presence of superconductivity[36].

There is a significant similarity with a model derived by Kadin[33], where he proposes a mechanism for superconductivity without pairing.

Kadin derived his model from the behaviour of charge density waves. He demonstrated that phenomena such as flux quantization do not require pair forming in order to give the proper values.

The relation of the alternative model to the BCS theory is shown in figure 6.3.

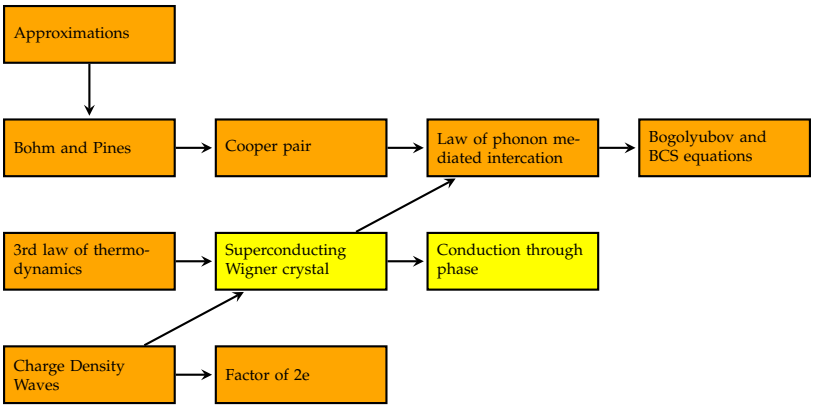


Figure 6.3.: Relation between alternative model and BCS theory

6.3. Quantitative

It might be rewarding to attempt to make this model more quantitative by using the Lindemann criterion. This criterion has been formulated to predict the melting point of solids. The freezing of electrons in a solid structure suggests that a similar approach might be appropriate to this situation.

The Lindemann criterion assumes that the average thermal energy can be estimated to be

$$E = k_B T = 4\pi^2 m f^2 u^2$$

Where k_B is the Boltzmann constant, T is the temperature, m is the atomic mass, f is the frequency and u is the average vibration amplitude.

Substituting $u^2 = c^2 a^2$, where c is the Lindemann constant and a is the atomic spacing, gives the melting point:

$$T_m = \frac{4\pi^2 m f^2 c^2 a^2}{k_B} \tag{6.1}$$

Other versions of this theorem use other estimates for the average thermal energy.

It should then be attempted to properly account for the charge of the electrons and the (periodic) charge distribution inside the material.

6.4. Experimental

To find out which model gives an accurate description of a superconductor, it might be required to perform some experiments.

Here we will discuss several observable properties that would follow from either one of these models.

6.4.1. Anti-ferromagnetic ordering of Cooper pairs

The Cooper pairs consist of two electrons, which circle in the same direction. This circulating current should generate a magnetic field. These fields are expected to interact with each other.

Ferromagnetic ordering is clearly not present in superconductors, since this would give an external field. However, it might be possible that for some reason the Cooper pairs would align in an anti-ferromagnetic way. This assumption seems reasonable since such a magnetic ordering is also found in the undoped cuprates, while a similar ordering of spin is found in the iron-based superconductors.

Therefore it might be good to look for magnetic fields of the size that would match those of a Cooper pair, in an anti-ferromagnetic ordering inside superconductors.

A 'ferromagneticlike' effect has been observed in $YBa_2Cu_3O_{6+x}$[37], but it was not determined whether the magnitude of the magnetic field is of a size that would be expected from a Cooper pair.

Additional experiments should be focussed on measuring the magnitude of magnetic fields on the scale of the coherence length.
Suitable experiments may be based on SQUIDS, which are capable of measuring very small variations in magnetic fields. The fact that squids themselves are based on superconductors might lead to problems when 'zooming in' to the right scale, since there possible fields from the squid itself may interfere.

6.4.2. Linear versus circular movement

A big difference between the two models is the electron movement. Cooper pairs require a circular movement, while the alternative model indicates a linear movement.
Therefore pairs might break easier by linear acceleration, while the alternative model might be more vulnerable to angular accelerations.

Such accelerations can be created when an external field generates a current. The surface current associated with the Meissner effect is linear, while the current around a flux vortex is circular.
A possible experiment could be to measure the maximum variation of a field per unit of time that does not break the superconductivity. The variations should be close to two reference fields: one below the first critical field (where the Meissner effect occurs) and one between the first and the second critical field (where flux vortices form).
The maximum acceleration of individual electrons in either the linear or the circular direction can then be calculated from this experiment.

6.4.3. Interaction with one or more 'partners'

Another difference is in the amount of electrons involved in the interaction with one electron. Taking a single electron out of the material would therefore give a different response from the material: In one case we might be left with one half Cooper pair that is incapable of interacting, because all other electrons are occupied. In the other case the crystal might rearrange itself to compensate for the local phase disturbance.

A way to take out one single electron might be to shoot a single particle (for example an electron or a photon) with sufficiently high energy at a superconductor in its ground state.
This should be done in such a way that it will hit just one electron, without giving energy to the other particles in the superconductor.

6.4.4. New superconductors

A way to support the new theory, that could be very useful at the same time, is to look for materials that, based on this theory would be superconducting.

Let us therefore formulate the hypothesis that in order to form a crystal structure of free electrons, we need:

- Free electrons
- A potential difference that prevents them from passing each other

The free electrons can most easily be obtained from a good conducting metal and the potential difference might follow from a high difference in electro-negativity between the atoms/ions.

A class of materials that is then expected to be superconducting, is that of **silver fluorides**: silver is a better conductor than copper and fluoride is more electronegative than oxide. The existence of superconductivity in these materials has also been suggested[38].

Whether this means that their critical temperatures will be even higher than those of cuprates can not be said in advance, since there will be more factors that influence the exact performance.

This is of course a simplified approach and it is not claimed that all materials consisting of a metal and atoms with very different electro-negativities will be superconductors, or that all other materials are not.

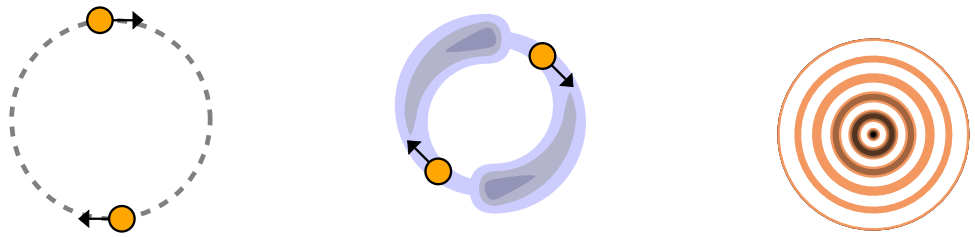
However, this might be a useful guideline in the search for new superconducting materials based on the alternative model.

7. Conclusion

7.1. Conclusion

Anderson's schematic picture of the BCS Cooper pair has been corrected, by assuming an identical circular motion of the electrons. This seems to be the only schematic representation that is able to sustain the attractive potential between two moving electrons. This representation also seems to fit the s-wave symmetry that is found with a more rigorous approach.

This cooper pair is visualized in figure 7.1. The schematic and classical picture clarify the BCS pairing mechanism, while the quantum-mechanical picture shows the s-wave symmetry that results from quantum effects.



(a) Schematic (b) Classical (c) Quantum-mechanical

Figure 7.1.: Representations for the Cooper pair

Maximum ordering, as predicted by the third law of thermodynamics, leads to a different model. In this model the 'free' electrons freeze into a Wigner crystal, which is forced by the ion potentials. The pairing mechanism is replaced by a two phase state. The phonon mediated interaction follows from ordering arguments, which makes it compatible with the present knowledge about conventional superconductors.

Arguments are given for the presence of superconductivity in such a structure, as a result of phase coherence between electrons.

It was argued that the most of the assumptions in the BCS model are not required to derive the BCS equations and that some of these assumptions might even be invalid. Assumptions like the jellium model, point-like interactions and the random phase approximation, which have been introduced to simplify the mathematics, seem to conspire to rule out alternative mechanisms that are equally capable of producing the BCS equations.

The alternative model shows great similarities with the Mott-insulators that play an essential role in high temperature superconductivity. Assuming that high temperature superconductors obey the same mechanism explains the electron-hole asymmetry and the interlayer coupling in these materials. It is suggested that critical temperatures could be increased, by using materials with larger internal differences in electronegativity, while still having a source of conduction electrons.

The differences between the models allow experiments that can determine which model is correct. Experiments have been proposed, that focus on magnetic behaviour of Cooper pairs, the different ways of electron movement in the models, the amount of partners with which the electrons interact or the prediction of a new class of superconductors.

The content of this thesis is represented in figure 7.2: the orange blocks represent existing steps in the model, that have been investigated; the yellow blocks show where this thesis has made a contribution and the red blocks indicate proposals for future research.

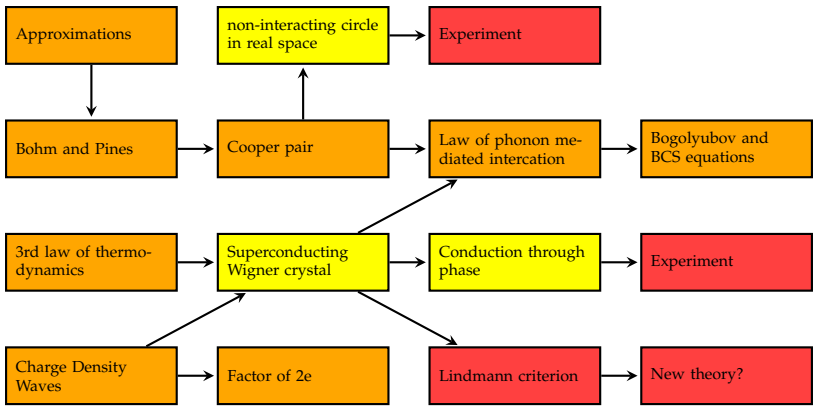
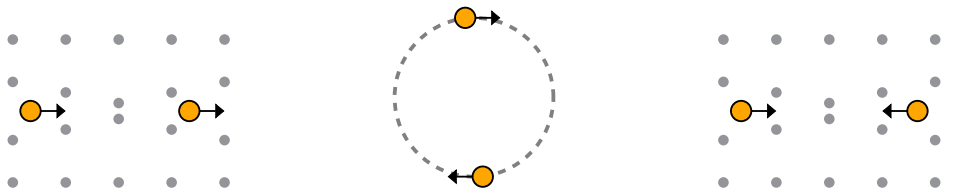


Figure 7.2.: Diagram of this thesis

To summarize, there have been three schematic representations of a superconducting electron pair in this thesis:



(a) Standard picture (b) BCS Cooper pair (c) Alternative model

Figure 7.3.: Models for an electron pair

Anderson's representation (figure 7.3a) was already known to be inconsistent. An alternative representation of the Cooper pair (figure 7.3b) has been investigated and it seems to be the only valid representation within the assumptions of the BCS model, so that physical inconsistencies in this representation should reflect flaws in the BCS model itself. The final representation (figure 7.3c) is derived from the third law of thermodynamics. It is compatible with the BCS equations, but it appears to apply for unconventional superconductors as well, where it offers an explanation for some of the phenomena that are not otherwise understood.

7.2. Recommendations

The BCS theory is likely to remain the standard until the validity of an alternative theory has been determined and possibly even after that (if it turns out to be correct after all). Therefore the first recommendation will be to explain the BCS pairing mechanism with a picture that is physically correct, so that everyone studying BCS theory will get a proper understanding of how the pairing mechanism works.

It is also recommended to pay attention to the limitations that result from assumptions made in deriving the BCS model. This way not only the mechanism itself, but also its validity will be better understood.

The second recommendation is to further develop the presented alternative model, so that more quantitative predictions can be made. A good start might be to modify the Lindemann criterion.

It should be attempted to apply this model not only to conventional, but also to unconventional superconductors. Here it might have added value over the BCS theory, if at least it turns out to be valid.

Furthermore, it should be attempted to search for the behaviour associated with either of the models experimentally.

Several suggestions for experiments have been given. These need to be worked out in more detail, so that reliable experiments can be developed.

And of course it is recommended to actually carry out some of the proposed experiments.

The BCS equations remain a powerful tool in conventional superconductivity, but the status of the underlying BCS model should be rethought, since it has some clear limitations that become obvious in real space.

The final recommendation is to those who still take the BCS theory for granted: Progress in science requires a critical look at all theories, even the old ones that are still considered to be successful. Theories are created in a certain historical and cultural context; they often contain assumptions that seemed reasonable at the time, but which might be outdated now due to new insights.

Take a close look at the BCS assumptions, such as the jellium model: The proof is in the pudding.

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A. Derivations

This part contains derivations for important equations in superconductivity. Only definitions and well known equations are used in the process (such as those from Maxwell, Newton and Schrödinger).

A.1. London theory

The first London equation can be derived by filling in the electric component of the Lorentz force in to Newtons second law, which is valid for the 'super electrons' that do not have any resistance

$$F = qE = ma$$

With the appropriate expressions for all quantities, this can be written as

$$-(n_s e)E = (n_s m_e)\left(\frac{dv_s}{dt}\right)$$

$$E = \left(\frac{m_e}{n_s e^2}\right)\frac{d(n_s e v_s)}{dt}$$

Defining $j_s = n_s e v_s$ and $\Lambda = m_e/n_s e^2$, gives the first london equation:

$$E = \Lambda \frac{dj_s}{dt} \tag{A.1}$$

The second london equation can be derived by taking the curl of the first london equation and filling in Maxwells law

$$\nabla \times E = \Lambda \nabla \times \frac{dj_s}{dt}$$

$$-\frac{dB}{dt} = \Lambda \nabla \times \frac{dj_s}{dt}$$

Integrating both sides gives the second london equation

$$B = -\Lambda \nabla \times j_s \tag{A.2}$$

This second equation can be rewritten using Amperes law, which will be rewritten, by taking the curl on both sides and rewriting the left side

$$\nabla \times B = \mu_0 j_s$$

$$\nabla \times (\nabla \times B) = \mu_0 \nabla \times j_s$$

$$\nabla(\nabla \cdot B) - \nabla^2 B = \mu_0 \nabla \times j_s$$

$$-\nabla^2 B = \mu_0 \nabla \times j_s$$

Filling in the second London equation gives

$$-\nabla^2 B = \mu_0 \left(-\frac{B}{\Lambda}\right)$$

$$B - \lambda^2 \nabla^2 B = 0 \tag{A.3}$$

With

$$\lambda = \sqrt{\frac{\Lambda}{\mu_0}} = \sqrt{\frac{m_e}{n_s e^2 \mu_0}} \tag{A.4}$$

Which in 1D has the solution

$$B(x) = B_0 e^{-x/\lambda}$$

It is also possible to write the relation with the vector potential from the second London equation:

$$B = \nabla \times A = -\Lambda \nabla \times j_s$$

Which can be integrated, choosing the integration constant 0

$$A = -\Lambda j_s + C$$

$$A = -\Lambda j_s \tag{A.5}$$

Using $\Lambda^{-1} = n_s e^2 / m_e$, the equations can be written in terms of the current like

$$\frac{dj_s}{dt} = \Lambda^{-1} E$$

$$\nabla \times j_s = -\Lambda^{-1} B$$

$$j_s = -\Lambda^{-1} A$$

A.2. Ginzburg-Landau and GLAG theory

A.2.1. Ginzburg-Landau equations

The derivation of the Ginzburg-Landau equations starts with a Taylor expansion for the firtst terms of the free energy:

$$F_{s0} = F_n + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4$$

Adding the quantum mechanical kinetic energy $\frac{p^2}{2m}$ gives

$$F_{s0} = F_n + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{|(-i\hbar\nabla)\Psi|^2}{2m^*}$$

Including the magnetic field in the momentum and as extra terms in the energy gives

$$F_{sH} = F_n + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{|(-i\hbar\nabla - 2eA)\Psi|^2}{2m^*} + \frac{B^2}{2\mu_0} - \frac{\mu_0 H^2}{2}$$

Substracting the normal free energy and integrating over the entire superconductor gives the Ginzburg-Landau functional:

$$F_{GL} = F_s - F_n = \int \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{|(-i\hbar\nabla - 2eA)\Psi|^2}{2m^*} + \frac{B^2}{2\mu_0} - \frac{\mu_0 H^2}{2} \cdot dV$$

Which can be rewritten to the Gibbs free energy:

$$G_{GL} = \int \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4 + \frac{|(-i\hbar\nabla - 2eA)\Psi|^2}{2m^*} + \frac{B^2}{2\mu_0} - \frac{\mu_0 H^2}{2} - B \cdot H \cdot dV \tag{A.6}$$

Minimizing with respect to Ψ^* gives the first Ginzburg Landau equation:

$$\alpha\Psi + \beta|\Psi|^2\Psi + \frac{1}{2m_c}(-i\hbar\nabla - 2eA)^2\Psi = 0 \tag{A.7}$$

Minimizing with respect to A gives the second Ginzburg Landau equation:

$$j_s = -\frac{i\hbar e}{m_c}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) - \frac{4e^2}{m_c}A|\Psi|^2 \tag{A.8}$$

The Ginzburg-Landau equation for the Gibbs free energy at an N/S interface can be rewritten as:

$$G_{GL} = \int_0^\infty \{\mu_0 H_c^2 \xi^2 (\frac{df}{dx})^2 + \frac{B}{2\mu_0}(B - \mu_0 H_c) + \frac{\mu_0}{2}(H^2 - H_c^2)\}dx$$

Which consists of three terms. The first two are most imprortant: They represent the loss in condensation energy and the relaxation magnetic energy.

$$G_{GL} = G_M(\xi) + G_E(\lambda)$$

A.2.2. Characteristic lengths

At a normal metal-superconductor interface the GL equations can be written as

$$-\xi^2\frac{d^2\Psi}{dx^2}+(\frac{2\pi\xi}{\Phi_0})^2A^2\Psi-\Psi+\Psi^3=0$$

$$\frac{d^2A}{dx^2}=(\frac{\Psi^2}{\lambda^2})A$$

The first can be reduced to:

$$-\xi^2\frac{d^2\Psi}{dx^2}-\Psi+\Psi^3=0$$

$$-\xi^2\frac{d^2\epsilon}{dx^2}-2\epsilon=0$$

With $\Psi=1-\epsilon$ and more important, the coherence length:

$$\xi=\sqrt{\frac{\hbar}{4m|\alpha|}} \tag{A.9}$$

The penetration depth can be written as:

$$\lambda=\sqrt{\frac{mc^2\beta}{8\pi e^2|\alpha|}} \tag{A.10}$$

We can also define:

$$\kappa=\lambda/\xi \tag{A.11}$$

A.2.3. Flux quantisation

The magnetic flux quantum follows from the periodicity of a wavefunction around a loop with flux passing through. It can be derived from the second Ginzburg Landau equation, setting the current to zero.

$$\frac{i\hbar e}{m_c}(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)=-\frac{4e^2}{m_c}A|\Psi_\infty|^2$$

We can simplify this using the expression

$$\Psi^*\nabla\Psi-\Psi\nabla\Psi^*=2i|\Psi_\infty|^2\nabla\varphi$$

Resulting in:

$$\frac{i\hbar e}{m_c}(2i|\Psi_\infty|^2\nabla\varphi)=-\frac{4e^2}{m_c}A|\Psi_\infty|^2$$

$$\hbar \nabla \varphi = 2eA$$

Integrating gives the flux

$$\oint \hbar \nabla \varphi \cdot dl = \oint 2eA \cdot dl$$

$$\frac{\hbar}{2e} \oint \nabla \varphi \cdot dl = \oint A \cdot dl = \int \nabla \times A \cdot dS = \int B \cdot dS = \Phi$$

We know that the phase changes with $n \cdot 2\pi$ when you integrate over a full circle. This gives the flux quantization:

$$\Phi = \frac{\hbar}{2e}(n \cdot 2\pi) = n \cdot \Phi_0$$

with

$$\Phi_0 = \frac{\pi\hbar}{e} = \frac{h}{2e} = 2.07 \times 10^{-15} Wb \tag{A.12}$$

A.2.4. Critical fields

The thermodynamic critical field can be expressed in terms of free energy, by considering the magnetization. The magnetic moment per volume of a superconductor compensates the external field and can therefore be written as:

$$M = -H_0/4\pi$$

The work needed to create this magentization gives the difference in free energy. It can be found by integrating over the total field:

$$W = \Delta F = \int_0^{H_0} -M \cdot dH_0 = \int_0^{H_0} H_0/4\pi \cdot dH_0 = H_0^2/8\pi$$

The critical field must require a difference in energy that corresponds to the difference between the superconducting ground state and the normal state:

$$\Delta F_{n,s} = F_n - F_{s0} = H_{cm}^2/8\pi$$

The Ginzburg-Landau equations give:

$$F_n - F_{s0} = \frac{\alpha^2}{2\beta}$$

If α and β are expressed in the characteristic lengths, then we can write the thermodynamic critical field in relation to the flux quantum:

$$H_{cm} = \frac{\Phi_0}{2\sqrt{2}\lambda\xi} \tag{A.13}$$

The field of a single vortex can be derived from the GL equation for the vector potential, which can be written as:

$$\nabla \times (\nabla \times A) = \frac{1}{\lambda^2}(\frac{\Phi_0}{2\pi}\nabla\phi - A)$$

$$\nabla \times H = \frac{1}{\lambda^2}(\frac{\Phi_0}{2\pi}\nabla\phi - A)$$

$$\lambda^2(\nabla \times H) = \frac{\Phi_0}{2\pi}\nabla\phi - A$$

$$\lambda^2\nabla \times (\nabla \times H) = \nabla \times (\frac{\Phi_0}{2\pi}\nabla\phi) - (\nabla \times A)$$

$$H + \lambda^2\nabla \times (\nabla \times H) = \frac{\Phi_0}{2\pi}\nabla \times (\nabla\phi)$$

There is only a phase change in the center of the vortex (delta function in the direction of the vortex), equal to 2π, so we can write:

$$H + \lambda^2\nabla \times (\nabla \times H) = \Phi_0\delta(r)e_v$$

Which, fot the boundary condition $H(\infty) = 0$, has the solution:

$$H = \frac{\Phi_0}{2\pi\lambda^2}K_0(r/\lambda)$$

Where K_0 can be written as $ln\kappa$, so that

$$H(0) = \frac{\Phi_0}{2\pi\lambda^2}ln\kappa$$

A more accurate calculation gives

$$H(0) = \frac{\Phi_0}{2\pi\lambda^2}(ln\kappa - 0.18) \tag{A.14}$$

The london expression for the free energy gives:

$$\epsilon = \frac{1}{8\pi}\int (H^2 + \lambda^2(\nabla \times H)^2) \cdot dV = \frac{\Phi_0}{8\pi}H(0) = (\frac{\Phi_0}{4\pi\lambda})^2(ln\kappa + 0.08)$$

The Gibbes free energy can be written as

$$G = \epsilon - \frac{\Phi_0 H_0}{4\pi}$$

Which becomes negative at the critical field, so that

$$H_{c1} = \frac{4\pi\epsilon}{\Phi_0}$$

Which can be written as:

$$H_{c1} = \frac{1}{\mu_0}\frac{\Phi_0}{4\pi\lambda^2}(ln\kappa + 0.08) \tag{A.15}$$

Two vortices in contact can be seen as being seperated by a thin film of thickness κ. The critical field for a thin film leads to the estimate:

$$H_{c2} = H_{cm}\lambda/d = H_{cm}\lambda/\xi = \kappa H_{cm}$$

More accurate calculations give:

$$H_{c2} = \sqrt{2}\kappa H_{cm} \tag{A.16}$$

A.2.5. Thin films: Fields

The magnetic field for a thin film can be derived using the second london equation. We choose a film in the x,y-plane and the magnetic field in the x-direction. Maxwells fourth equation gives the current in the y-direction:

$$\frac{\partial B_x}{\partial z} = \mu_0 j_y$$

We can find the magnetic field by solving the second London equation for the boundary conditions $B_x = B_0$ at $z = \pm d/2$. Which gives a standard solution

$$B - \lambda^2\nabla^2 B = 0$$

$$B_x = B_0\frac{cosh(z/\lambda)}{cosh(d/2\lambda)}$$

$$j_y = \frac{1}{\mu_0}\frac{\partial B_x}{\partial z} = \frac{B_0}{\lambda\mu_0}\frac{sinh(z/\lambda)}{cosh(d/2\lambda)}$$

If we let the current generate the magnetic field, in stead of the other way around, the boundary condition changes to $B_1 = I/2$ at $z = \pm d/2$, resulting in:

$$B_x = B_1\frac{sinh(z/\lambda)}{cosh(d/2\lambda)}$$

$$j_y = \frac{1}{\mu_0}\frac{\partial B_x}{\partial z} = \frac{B_1}{\lambda\mu_0}\frac{cosh(z/\lambda)}{cosh(d/2\lambda)}$$

For $d << \lambda$ this simplifies to:

$$B_x = I\frac{z}{d} \tag{A.17}$$

$$j_y = \frac{I}{d} \tag{A.18}$$

A.2.6. THIN FILMS: INDUCTANCE

The inductance per square can be deremined by equating the stored energy

$$E_L = \frac{1}{2}LI^2$$

With the magnetic and kinetic energy:

$$E_M = \int_z \frac{1}{2}B^2 \cdot dz$$

$$E_K = \int_z \frac{1}{2}mv^2 \cdot dz = \int_z \frac{1}{2}\lambda^2 j_y^2 \cdot dz$$

The magnetic and kinetic inductance per square are then given by:

$$L^M = \frac{1}{I^2}\int_0^\infty B_x^2 dz$$

$$L^K = \frac{\lambda^2}{I^2}\int_0^\infty j_y^2 dz$$

For a semi-infinite superconductor the field and current are given by:

$$B_x = \mu_0 J e^{-z/\lambda}$$

$$j_y = \frac{\mu_0 J}{\lambda}e^{-z/\lambda}$$

This results in:

$$L^M = L^K = \mu_0\lambda/2 \tag{A.19}$$

For the thin film derived above, the result is:

$$L^M = \frac{1}{I^2}\int_0^\infty B_x^2 dz = \frac{d}{12} \tag{A.20}$$

$$L^K = \frac{\lambda^2}{I^2}\int_0^\infty j_y^2 dz = \frac{\lambda^2}{d} \tag{A.21}$$

So for $d << \lambda$:

$$L^K >> L^M$$

A.3. BCS THEORY

This derivation is based on the Schmidt's book [3].

BCS theory will be derived from the assumption interactions only occur if there is sufficient energy available in the vibrations. This means that $V_{kk'} = 0$ except for electrons with an energy no more than $\hbar\omega_D$ from the Fermi energy, where the attractive potential can be defined negative as:

$$V_{kk'} = -V$$

To calculate the energy of the superconductor, we will use the following quantum-mechanics:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = E_{kin} + V$$

$$V = \langle \Psi | \hat{V} | \Psi \rangle = \left\langle \sum_n a_n \Psi_n \middle| \hat{V} \middle| \sum_m a_m \Psi_m \right\rangle = \sum_{n,m} a_n^* a_m V_{nm}$$

$$V_{nm} = \langle \Psi_n | \hat{V} | \Psi_m \rangle$$

A.3.1. ENERGY MINIMUM

The probability of an occupied pair will be denoted with v_k^2 and we define $u_k^2 = 1 - v_k^2$. This will give the energy of a superconductor

$$a_n = \sqrt{v_k^2(1 - v_{k'}^2)} = v_k u_{k'} \qquad a_m = \sqrt{v_{k'}^2(1 - v_k^2)} = v_{k'} u_k$$

Using the definition

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k_F^2}{2m}$$

Gives

$$E_s = E_{kin,total} + V_{mean} = \sum_k 2\varepsilon_k v_k^2 + \sum_{k,k'} V_{kk'} v_k u_k v_{k'} u_{k'} \tag{A.22}$$

The minimum value of the energy corresponds to $\partial E_s / \partial v_k^2 = 0$, which gives the result

$$2\varepsilon_k - V \frac{1 - 2v_k^2}{v_k u_k} \sum_{k'}{}' v_{k'} u_{k'} = 0$$

$$\frac{v_k u_k}{1 - 2v_k^2} = \frac{\Delta_0}{2\varepsilon_k} \tag{A.23}$$

$$v_k^4 - v_k^2 + \frac{\Delta_0^2}{4E_k^2} = 0$$

Where the $'$ denotes that we only take a layer near the Fermi surface and

$$\Delta_0 = V\sum_{k'}' v_{k'} u_{k'} \tag{A.24}$$

$$E_k = \sqrt{\varepsilon_k^2 + \Delta_0^2} \tag{A.25}$$

Using this again gives

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\varepsilon_k}{E_k}\right) \tag{A.26}$$

A.3.2. Gap

The expression for v_k^2 can be used to find the value of Δ_0

$$\Delta_0 = V\sum_{k'}' \sqrt{\frac{1}{2}\left(1 - \frac{\varepsilon_k}{E_k}\right)\frac{1}{2}\left(1 + \frac{\varepsilon_k}{E_k}\right)}$$

$$\Delta_0 = \frac{V}{2}\sum_{k'}' \sqrt{\frac{E_k^2 - \varepsilon_k^2}{E_k^2}} = \frac{V\Delta_0}{2}\sum_{k'}' \sqrt{\varepsilon_k^2 + \Delta_0^2}$$

$$\frac{1}{V} = \frac{1}{2}\sum_{k'}' \sqrt{\varepsilon_k^2 + \Delta_0^2}$$

Here we introduce the formula

$$\sum_{k'}' \cdots = \int_{-\hbar\omega_D}^{\hbar\omega_D} \cdots N(\varepsilon)\cdot d\varepsilon$$

So that

$$\frac{1}{N(0)V} = \frac{1}{2}\int_{-\hbar\omega_D}^{\hbar\omega_D} \sqrt{\varepsilon_k^2 + \Delta_0^2}\cdot d\varepsilon = \int_{0}^{\hbar\omega_D} \sqrt{\varepsilon_k^2 + \Delta_0^2}\cdot d\varepsilon = \operatorname{arcsin}\left(\frac{\hbar\omega_D}{\Delta_0}\right)$$

$$\frac{\hbar\omega_D}{\Delta_0} = \sinh\left(\frac{1}{N(0)V}\right)$$

Which for low values of $N(0)V$ reduces to

$$\Delta_0 \simeq 2\hbar\omega_D\, e^{-1/N(0)V} \tag{A.27}$$

A.3.3. GROUND STATE ENERGY

The ground state energy is given by

$$W = E_s - E_n = \left[\sum_k 2\varepsilon_k v_k^2 + \sum_{k,k'} V_{kk'} v_{k'} u_k v_k u_{k'}\right] - \left[\sum_{k<k_F} 2\varepsilon_k\right]$$

$$W = \sum_{k<k_F} 2\varepsilon_k (v_k^2 - 1) + \sum_{k>k_F} 2\varepsilon_k v_k^2 - V{\sum_{k,k'}}' v_k u_k v_{k'} u_{k'}$$

$$W = \sum_{k<k_F} |\varepsilon_k| \left(1 - \frac{|\varepsilon_k|}{E_k}\right) + \sum_{k>k_F} \varepsilon_k \left(1 - \frac{\varepsilon_k}{E_k}\right) - V{\sum_{k,k'}}' v_k u_k v_{k'} u_{k'}$$

$$W = 2\sum_{k>k_F} \varepsilon_k \left(1 - \frac{\varepsilon_k}{E_k}\right) - V{\sum_{k,k'}}' v_k u_k v_{k'} u_{k'}$$

Using the definition of Δ_0 leads to

$${\sum_{k,k'}}' v_k u_k v_{k'} u_{k'} = \frac{\Delta_0^2}{V^2}$$

Which can be used, so that

$$W = 2\sum_{k>k_F} \varepsilon_k \left(1 - \frac{\varepsilon_k}{E_k}\right) - \frac{\Delta_0^2}{V^2}$$

$$W = 2N(0) \int_0^{\hbar\omega_D} \varepsilon \left(1 - \frac{\varepsilon}{\sqrt{\varepsilon_k^2 + \Delta_0^2}}\right) d\varepsilon - \frac{\Delta_0^2}{V^2}$$

$$W = N(0)\Delta_0^2 \left[\left(\frac{\hbar\omega_D}{\Delta_0}\right)^2 - \frac{\hbar\omega_D}{\Delta_0}\sqrt{1 + \left(\frac{\hbar\omega_D}{\Delta_0}\right)^2} + \operatorname{arcsin}\frac{\hbar\omega_D}{\Delta_0}\right] - \frac{\Delta_0^2}{V^2}$$

$$W = -\frac{1}{2}N(0)\Delta_0^2 \tag{A.28}$$

A.3.4. CRITICAL FIELD

Using the expression relating the superconducting state energy to the critical field gives

$$W = -\frac{1}{2}N(0)\Delta_0^2 \qquad W = -\frac{H_{cm}^2(0)}{8\pi}$$

$$H_{cm}(0) = \Delta_0\sqrt{4\pi N(0)} \tag{A.29}$$

A.3.5. Single pair

The energy contribution of a single pair is given by

$$w_q = 2\varepsilon_q v_q^2 - 2V v_q u_q \sum_{k'}{}' v_k u_k$$

$$w_q = 2\varepsilon_q \frac{1}{2}\left(1 - \frac{\varepsilon_q}{E_q}\right) - 2\sqrt{\frac{1}{4}\left(1 - \frac{\varepsilon_q^2}{E_q^2}\right)}\Delta_0$$

$$w_q = \varepsilon_q - \frac{\varepsilon_q^2}{E_q} - \frac{\Delta_0^2}{E_q} = \varepsilon_q - E_q$$

The energy of the superconductor will change with

$$W_q = W - w_q + \varepsilon_q = W + E_q$$

$$W_q = W + \sqrt{\varepsilon_q^2 + \Delta_0^2} \tag{A.30}$$

So the energy will change with at least Δ_0, which therefore must represent an energy gap.

A.3.6. Density of states

The density of states can be calculated with

$$\rho(E) = \frac{d\nu}{dE} = \frac{d\nu}{d\varepsilon}\frac{d\varepsilon}{dE}$$

For metals $d\nu/d\varepsilon = N(0)$ and $d\varepsilon/dE$ can be calculated from E, so that

$$\rho(E) = N(0)\frac{E}{\sqrt{E^2 - \Delta_0^2}} \tag{A.31}$$

A.3.7. Coherence length

The uncertainty in the momentum is given by

$$\Delta p = \hbar \Delta k \sim \hbar\left(2\Delta_0 \frac{k_F}{\varepsilon_F}\right)$$

This gives the uncertainty in position, which also represents the coherence length

$$\xi_0 = \Delta x \sim \frac{1}{\Delta p} \sim \frac{\varepsilon_F}{2\hbar\Delta_0 k_F} = \frac{\hbar v_F}{4\Delta_0} = \frac{\hbar v_F}{4\Delta_0}$$

Using the expression for Δ_0 in a rigorous calculation gives

$$\xi_0 = 0.18\frac{\hbar v_F}{k_B T_c} \tag{A.32}$$

A.3.8. Finite Temperature

The probability that a state is occupied can be calculated with Fermi-Dirac statistics

$$f_k = \frac{1}{e^{E_k/k_B T}+1}$$

The chance that a pair state is unoccupied is then $1-2f_k$, so that the energy can be written as

$$W = \sum_k 2|\varepsilon_k| f_k + 2\sum_k \varepsilon_k(1-2f_k)v_k^2 - V\sum_{k,k'}{}' v_k u_k v_{k'} u_{k'}(1-2f_k)(1-2f_{k'})$$

The free energy is $F = W - TS$ and the minimum is at $\partial F/\partial v_q^2 = 0$ Resulting in a similar derivation as before:

$$\frac{v_k u_k}{1-2v_q^2} = \frac{\Delta}{2\varepsilon_k}$$

$$\Delta = V\sum_{k'}{}' v_k u_k (1-2f_k)$$

$$v_q^2 = \frac{1}{2}\left(1-\frac{\varepsilon_q}{E_q}\right)$$

$$E_q = \sqrt{\varepsilon_q^2 + \Delta_0^2(T)}$$

Which now gives the results

$$\Delta = V\sum_{k'}{}' \frac{\Delta}{2E_k}\left(1-\frac{2}{e^{E_k/k_B T}+1}\right)$$

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{\sqrt{\varepsilon_k^2+\Delta_0^2(T)}} \tanh\frac{\sqrt{\varepsilon_k^2+\Delta_0^2(T)}}{2k_B T}$$

There is no gap at the critical temperature, so we can write

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega_D} \frac{d\varepsilon}{\varepsilon}\tanh\frac{\varepsilon}{2k_B T_c}$$

$$k_B T_c = 1.14\hbar\omega_D e^{-1/N(0)V} \tag{A.33}$$

The dependence on ω gives the isotope effect, because $\omega_D \propto \sqrt{M}$. Using the expression for the gap at 0K derived earlier gives

$$2\Delta_0 = 3.52 k_B T_c \tag{A.34}$$

A.4. JOSEPHSON

The Schrödinger equation can be modified to contain coupling between two wavefunctions

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

$$i\hbar \frac{\partial \Psi_1}{\partial t} = \frac{e^* V}{2}\Psi_1 + \kappa \Psi_2$$

The derivative of the superconducting wave-function $\Psi = \sqrt{n_s}e^{i\varphi}$ can be rewritten using the product rule and the chain rule

$$\frac{\partial \Psi}{\partial t} = \frac{\partial \sqrt{n_s} e^{i\varphi} i}{\partial t}$$

$$\frac{\partial \Psi}{\partial t} = \frac{\partial \sqrt{n_s}}{\partial t} e^{i\varphi} + \frac{\partial e^{i\varphi}}{\partial t}\sqrt{n_s}$$

$$\frac{\partial \Psi}{\partial t} = \frac{1}{2\sqrt{n_s}}\frac{\partial n_s}{\partial t}e^{i\varphi} + ie^{i\varphi}\frac{\partial \varphi}{\partial t}\sqrt{n_s} = \left[\frac{1}{2\sqrt{n_s}}\frac{\partial n_s}{\partial t} + i\sqrt{n_s}\frac{\partial \varphi}{\partial t}\right]e^{i\varphi}$$

Putting this in the coupled Schrödinger equation and dividing everything by $e^{i\varphi_1}$ gives

$$i\hbar\left[\frac{1}{2\sqrt{n_{s_1}}}\frac{\partial n_{s_1}}{\partial t} + i\sqrt{n_{s_1}}\frac{\partial \varphi}{\partial t}\right]e^{i\varphi_1} = \frac{e^* V}{2}\sqrt{n_{s_1}}e^{i\varphi_1} + \kappa\sqrt{n_{s_2}}e^{i\varphi_2}$$

$$i\hbar\left[\frac{1}{2\sqrt{n_{s_1}}}\frac{\partial n_{s_1}}{\partial t} + i\sqrt{n_{s_1}}\frac{\partial \varphi}{\partial t}\right] = \frac{e^* V}{2}\sqrt{n_{s_1}} + \kappa\sqrt{n_{s_2}}\frac{e^{i\varphi_2}}{e^{i\varphi_1}}$$

The last term can be rewritten with Euler's rule, using $\varphi_2 - \varphi_1 = \Delta\varphi$

$$\frac{e^{i\varphi_2}}{e^{i\varphi_1}} = e^{i(\varphi_2 - \varphi_1)} = e^{i(\Delta\varphi)} = \cos\Delta\varphi + i\sin\Delta\varphi$$

Filling this in and carrying out the multiplications results in

$$i\hbar\left[\frac{1}{2\sqrt{n_{s_1}}}\frac{\partial n_{s_1}}{\partial t} + i\sqrt{n_{s_1}}\frac{\partial \varphi}{\partial t}\right] = \frac{e^* V}{2}\sqrt{n_{s_1}} + \kappa\sqrt{n_{s_2}}(\cos\Delta\varphi + i\sin\Delta\varphi)$$

$$\frac{i\hbar}{2\sqrt{n_{s_1}}}\frac{\partial n_{s_1}}{\partial t} - \hbar\sqrt{n_{s_1}}\frac{\partial \varphi_1}{\partial t} = \frac{e^* V}{2}\sqrt{n_{s_1}} + \kappa\sqrt{n_{s_2}}\cos\Delta\varphi + \kappa\sqrt{n_{s_2}}i\sin\Delta\varphi$$

The imaginary part of this last equation gives

$$\frac{i\hbar}{2\sqrt{n_{s_1}}}\frac{\partial n_{s_1}}{\partial t} = \kappa\sqrt{n_{s_2}}i\sin\Delta\varphi$$

$$\frac{\partial n_{s_1}}{\partial t} = \frac{2\kappa\sqrt{n_{s_1}n_{s_2}}}{\hbar}\sin\Delta\varphi$$

It is known that the term on the left represents the current. The pre-factor of the sine represents the amplitude of the variable current. Therefore this equation can be written as

$$I = I_c\sin\Delta\varphi \tag{A.35}$$

The real part of the equation gives

$$-\hbar\sqrt{n_{s_1}}\frac{\partial\varphi_1}{\partial t} = \frac{e^*V}{2}\sqrt{n_{s_1}} + \kappa\sqrt{n_{s_2}}\cos\Delta\varphi$$

$$\frac{\partial\varphi_1}{\partial t} = -\frac{e^*V}{2\hbar}\sqrt{n_{s_1}} - \frac{\kappa}{\hbar}\sqrt{\frac{n_{s_2}}{n_{s_1}}}\cos\Delta\varphi$$

A similar derivation can be done for $\frac{\partial\varphi_2}{\partial t}$, with the same $\Delta\varphi$ (Because $\cos(-\Delta\varphi) = \cos(\Delta\varphi)$), but the reversed coupling will result in a different sign in front of the first term on the right side:

$$\frac{\partial\varphi_2}{\partial t} = +\frac{e^*V}{2\hbar}\sqrt{n_{s_2}} - \frac{\kappa}{\hbar}\sqrt{\frac{n_{s_1}}{n_{s_2}}}\cos(\Delta\varphi)$$

Subtracting the previous equation from this one gives the change in phase difference:

$$\frac{\partial\varphi_2}{\partial t} - \frac{\partial\varphi_1}{\partial t} = \left[+\frac{e^*V}{2\hbar}\sqrt{n_{s_2}} - \frac{\kappa}{\hbar}\sqrt{\frac{n_{s_1}}{n_{s_2}}}\cos(\Delta\varphi)\right] - \left[-\frac{e^*V}{2\hbar}\sqrt{n_{s_1}} - \frac{\kappa}{\hbar}\sqrt{\frac{n_{s_2}}{n_{s_1}}}\cos(\Delta\varphi)\right]$$

$$\frac{\partial\Delta\varphi}{\partial t} = \frac{e^*V}{\hbar} + \left[\sqrt{\frac{n_{s_2}}{n_{s_1}}} - \sqrt{\frac{n_{s_1}}{n_{s_2}}}\right]\frac{\kappa}{\hbar}\cos(\Delta\varphi)$$

For $n_{s_1} = n_{s_2}$ this simplifies to the second Josephson equation:

$$\frac{\partial\Delta\varphi}{\partial t} = \frac{e^*V}{\hbar} \tag{A.36}$$

A.5. INTERFERENCE

Here we will look at interference between phase coherent electrons. For this purpose, let us look at what happens when two superconducting (groups of) electrons with different phases are added:

$$\Psi = \Psi_1 + \Psi_2 \qquad \Psi_1 = \sqrt{n_1}e^{i\varphi_1} \qquad \Psi_2 = \sqrt{n_2}e^{i\varphi_2}$$

$$\begin{aligned}
\langle\Psi|\Psi\rangle &= \langle\Psi_1|\Psi_1\rangle + \langle\Psi_1|\Psi_2\rangle + \langle\Psi_2|\Psi_1\rangle + \langle\Psi_2|\Psi_2\rangle \\
&= \left\langle \sqrt{n_1}e^{i\varphi_1} | \sqrt{n_1}e^{i\varphi_1} \right\rangle + \left\langle \sqrt{n_1}e^{i\varphi_1} | \sqrt{n_2}e^{i\varphi_2} \right\rangle \\
&\quad + \left\langle \sqrt{n_2}e^{i\varphi_2} | \sqrt{n_1}e^{i\varphi_1} \right\rangle + \left\langle \sqrt{n_2}e^{i\varphi_2} | \sqrt{n_2}e^{i\varphi_2} \right\rangle \\
&= n_1 + n_2 + \sqrt{n_1 n_2}\left\langle e^{i\varphi_1} | e^{i\varphi_2} \right\rangle + \sqrt{n_1 n_2}\left\langle e^{i\varphi_2} | e^{i\varphi_1} \right\rangle \\
&= n_1 + n_2 + \sqrt{n_1 n_2}\left[\left\langle e^{i\varphi_1} | e^{i\varphi_2} \right\rangle + \left\langle e^{i\varphi_2} | e^{i\varphi_1} \right\rangle\right] \\
&= n_1 + n_2 + \sqrt{n_1 n_2}\left[e^{i(\varphi_2-\varphi_1)} + e^{i(\varphi_1-\varphi_2)}\right] \\
&= n_1 + n_2 + \sqrt{n_1 n_2}\left[e^{i(\varphi_2-\varphi_1)} + e^{-i(\varphi_2-\varphi_1)}\right] \\
&= n_1 + n_2 + \sqrt{n_1 n_2}\left[2\cos(\varphi_2 - \varphi_1)\right]
\end{aligned}$$

Rewriting $\varphi_2 - \varphi_1 = \Delta\varphi$, $n = n_1 + n_2$ and $\langle\Psi|\Psi\rangle = \rho$ and taking $n_1 = n_2$(Valid when we take the average phase difference) gives

$$\rho = n + n\cos(\Delta\varphi) \tag{A.37}$$

Which is a standard result for interference.