Connecting the Microscopic and Macroscopic in Unconventional Superconductors

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Declaration

This thesis is an account of research undertaken between March 2017 and March 2018 at The Department of Physics, Division of sciences, Otago University, Dunedin, New Zealand.

The technique and results outlined in Chapter 4, sections 4.1.1-4.3.1 of this thesis were originally developed as part of my 2016 Honours dissertation.

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

Allyn M. Robins
March, 2018
Acknowledgements

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Abstract

In this thesis, a Linked-Cluster Expansion is utilized to derive expressions for the macroscopic Ginzburg-Landau constants in terms of variables connected to the microscopic Bogoliubov Hamiltonian. The resultant Ginzburg-Landau free energy is then numerically minimized in order to study the existence of a local Time-Reversal symmetry breaking state existing at the surface of a superconductor in which both triplet and singlet Cooper pairs can form. Both centrosymmetric and non-centrosymmetric systems are considered. These states are deemed physically achievable, and other features of the system are described and analysed. A brief history of superconductivity and primers on basic techniques used in the examination of many-particle quantum systems are also included. This investigation was motivated by the microscopic study of similar systems by C. Timm, S. Rex, and P. M. R. Brydon in the paper “Surface Instability in Nodal Noncentrosymmetric Superconductors”, published in Phys. Rev. B. vol 91, p. 180503(R), 2015. Although we use a substantially different approach to the problem, we obtain results in great qualitative agreement with Timm et al., as well as providing additional insight into the origin of the local Time-Reversal symmetry breaking state at the surface.
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Chapter 1

Introduction

Superconductivity is not nearly as mysterious today as it was when it was first discovered. But while we now have a good understanding of its most common forms, the properties and behaviours of many so-called ‘unconventional’ superconductors still lack a detailed theoretical description. This thesis examines a specific set of unconventional superconductors by using a Linked-Cluster Expansion to build a macroscopic simulation of superconductor behaviour that is derived from a microscopic Hamiltonian.

1.1 A Brief History of Superconductivity

In 1911 the celebrated Dutch physicist Heike Kamerlingh Onnes, cooling a solid mercury wire with the liquid helium that he had recently discovered how to produce, found to his astonishment that all resistivity in the material disappeared below 4.2 K. He swiftly proved that this strange new effect was not limited to mercury, however: both tin and lead, once cooled past unique temperatures, displayed this unheard-of behaviour. This complete disappearance of resistivity is known as ‘Perfect Conductivity’. It has been estimated that to detect any change in the current within an isolated ring of superconducting material, we would have to wait anywhere from $10^4$ to $10^{10}$ years [1].

1.1.1 Early Discoveries

This was a revelation without precedent or explanation. No existing theory had predicted anything like what Onnes had observed, but there was more to come. Twenty-two years after Onnes’ first breakthrough was recorded, as theorists continued to struggle to make sense of what he had discovered, another startling property of superconductors was revealed. The German physicists Fritz Walther Meissner and Robert Ochsenfeld, working in 1933, found that not only could no magnetic field enter a superconductor, but that any magnetic fields present in the material were expelled when the material entered its superconducting state [2].

This could not be explained as a consequence of the aforementioned ‘Perfect Conductivity’, and it was thus surmised that the superconductors were somehow creating a magnetic field that perfectly cancelled out all fields external to the material. In other words, in addition to being a perfect conductor, superconductors appeared to be perfect diamagnets. The sudden appearance of perfect diamagnetism occurring at the onset of superconductivity was termed the *Meissner-Ochsenfeld Effect*, usually shortened to the *Meissner Effect*.

Following quickly on the heels of this discovery was the conjecture that a sufficiently large magnetic field would destroy the superconducting state of a material it was applied
to. This was quickly confirmed, with the strength of the field required being found to depend parabolically on how far below its critical temperature the material was [1].

No less significant than these revelations, though less dramatic, was the observation that the constant-volume specific heat $C_V$ of superconducting materials abruptly increases at the critical temperature. This is indicative of a sharp decrease in entropy, which implies that a spontaneous ordering of some kind takes place in the transition to a superconducting state [2].

In the decades following Onnes, Ochsenfeld, and Meissner’s discoveries, many materials were demonstrated to possess the properties that they had described. But it was not until 46 years after Onnes’s initial discovery that a theory was developed that could adequately explain them.

1.1.2 The BCS Theory

In 1957, John Bardeen, Leon Cooper and John Schrieffer published a pair of papers simply entitled “Theory of Superconductivity” and “Microscopic Theory of Superconductivity” [3,4]. In these papers, they proposed a detailed model of superconductivity based on the existence of attractive interactions between electrons mediated by lattice vibrations.

An extremely simplified version of their thesis is as follows: When a negatively-charged electron moves through a lattice of positively-charged ions, it attracts them just as they attract it. This causes the ions to move fractionally toward the electron. However by the time the ions have moved, the electron will no longer be in the same place. Thus there is now a region of the lattice that more ions are close to, giving the region a net positive charge. Another electron will be attracted to this region, essentially causing an attractive force between the electrons mediated by vibrations in the positively charged lattice (or ‘phonons’). This overcomes Coulomb repulsion and binds the electrons together in loosely-correlated pairs.

A pair of electrons bound in this way is referred to as a ‘Cooper pair’ [5]. The attraction between the two electrons, while acting over long distances due to its mediation via the lattice, is very weak. This means that the binding energy of the Cooper pairs will be small, and thus the individual Cooper pairs themselves will be extremely large. They will therefore overlap with many others. This overlap of many correlated quantum pairs causes all of the electrons in Cooper pairs to act as a single ‘condensed’ macroscopic quantum state. This is somewhat analogous to Bose-Einstein condensation.

Due to the ‘condensed’ nature of the Cooper pairs, breaking one apart - for instance, in one of the scattering events that cause resistivity in materials - will affect the energy of all of the others. Thus to break apart a single pair would entail the breaking of a significant portion of the collective group. The energy required to do this is greater than can be provided by any individual scattering event, and so all of the electrons in Cooper pairs can effectively move without experiencing scattering. Thus the resistivity of the material disappears. The Meissner effect, according to the BCS theory, is due to spontaneous superconducting currents that generate a magnetic field exactly opposite to the field that would classically be present in the superconductor.

There are two key assumptions made by Bardeen, Cooper and Schrieffer in their theory. The first is that the Cooper pairs that form in the material have angular momentum $l = 0$, which corresponds to an $s$-wave, spin-singlet pairing state. The second is that the attractive interaction between the electrons is entirely mediated by phonons. These assumptions were accurate for all known superconductors at the time, and all that were
to be discovered for over two decades. This allowed the BCS theory to explain virtually every property of the superconductors researchers encountered.

However, we know today of a significant number of superconductors in which the Cooper pairs originate from some mechanism other than phonon interaction, or have angular momentums \( l > 0 \) \([6]\) \([7]\). These are the so-called ‘unconventional’ superconductors.

### 1.1.3 Unconventional Superconductors

The first indication that perhaps not all could be explained by the BCS theory came in 1972, when researchers realised the Helium-3 superfluid at a temperature of 2.5 mK. This had previously been thought impossible, as the condensation mechanism that causes ‘traditional’ superfluidity is only applicable to bosons like Helium-4 \([8]\). However, the fermionic Helium-3 atoms were forming pair-bound states analogous to Cooper pairs in a superconductor and thus forming a superfluid.

This was understandably startling, as both of the key assumptions made by Bardeen, Cooper and Schrieffer were called into serious question. The proposed Helium-3 ‘Cooper pairs’ could not be formed by the mechanism they had described, as there is no underlying lattice in a fluid to enable the phonon-mediated interaction at the core of the BCS theory. In addition, individual Helium-3 atoms are neutral, which would preclude any interactions based on charge even were a lattice to be present. Instead Helium-3 atoms are bound into Cooper pairs by the exchange of magnetic fluctuations, resulting in an angular momentum \( l = 1 \) spin-triplet state \([9]\).

Nevertheless, the BCS theory was largely unscathed by this discovery. The apparently unique nature of the Helium-3 superfluid and its lack of a lattice made any relevance to superconducting solids tenuous, and possible challenges to the BCS theory largely conjecture. It was six years later, in 1978, that an actual family of superconductors was found that seemed to contradict the key assumptions of the BCS theory.

These were the ‘Heavy Fermion’ superconductors, so-called because of the extremely large measured masses of their charge carriers. These ‘Heavy Fermions’ are typically Cerium- and Uranium-based compounds. The Cooper pairs that form in these materials have angular momentum \( l > 0 \), and their specific heat capacities \( C_V \) behave significantly differently to those of traditional BCS superconductors \([10]\). Nevertheless, their extremely low critical temperatures \( T_c \leq 2 \text{ K} \) made them difficult prospects for prolonged study.

It was not until eight years after the ‘Heavy Fermions’ were documented that ‘unconventional’ superconductors became the subject of intense scrutiny. This was due to the 1986 discovery of the ‘Cuprates’: superconductors composed of compounds containing stacked quasi-2D \( \text{CuO}_2 \)-planes \([11]\). Some of these superconductors had critical temperatures far higher than any ever discovered before: up to \( \sim 150 \text{ K} \), compared to the previous maximum of \( \sim 20 \text{ K} \) \([12–14]\).

Naturally, the world of superconductivity research was shaken by this discovery. The critical temperatures of these Cuprates completely precluded phonon-mediated Cooper pairing, as the necessary vibrations would have destroyed the lattice structure. The likeliest explanation seemed to be that magnetic fluctuations - similarly to the Helium-3 superfluid - were taking on the role of phonons in binding Cooper pairs, as the superconductivity observed occurs under conditions very close to those that change the material into an antiferromagnet. Although the pairing mechanism remains controversial, the Cooper pairs in these materials are generally understood to have angular momentum \( l = 2 \), implying a spin-singlet \( d \)-wave state \([15]\). Nevertheless, a complete theoretical picture of
superconductivity in Cuprates has yet to be constructed [16].

Since 1986, many more families of ‘unconventional’ superconductors have been discovered [6]. All have properties that cannot be explained using the BCS theory, and the search for a unifying ‘grand theory’ of superconductivity has so far borne no fruit. There is no particular phenomenological property that unites the so-called ‘unconventional’ superconductors save their inexplicability within the BCS framework. Some, for instance, have far higher critical temperatures than conventional superconductors, others far lower. However, it is possible to classify ‘unconventional’ superconducting states in terms of crystal symmetries. All ‘unconventional’ superconductors have properties that rely on the symmetries present in their lattices [17]. If two superconducting states transform differently under the same crystal symmetries, they will behave differently, and can be considered distinct.

1.2 Symmetries

There are many symmetries that can be used to distinguish different kinds of unconventional superconductivity: rotational symmetry, mirror symmetry, etc. However, there are only two symmetries that we will concern ourselves with in any detail.

The first is inversion symmetry. A crystal has inversion symmetry if there is some point around which all of its components can be inverted to produce the same arrangement of ions [18]. This can be thought of as applying one mirroring operation along each dimension. An example of a cell that breaks inversion symmetry is given in Fig. 1.1. Applying inversion to the system reverses the position vector \( r \rightarrow -r \), and thus the momentum is also reversed \( (k \rightarrow -k) \). The spin \( s \) is not affected as it behaves as an angular momentum \( \propto r \times k \). Thus for a physical quality \( f(r, k, s) \) if

\[
f(r, k, s) = f(-r, -k, s),
\]

then \( f \) is said to be invariant under inversion. The operation of inversion is a unitary transformation.

A less intuitive form of symmetry is Time-Reversal symmetry. A physical system is said to be symmetric under time-reversal if it evolves backwards in time in the same way by which it evolves forwards in time, i.e. reversing the flow of time would cause the system to trace through all its previous states. The position vector does not change under Time-
Reversal, but momentum is reversed \((k \rightarrow -k)\) as it is a time-derivative. Thus spin is also reversed. A physical quantity \(f(r, k, s)\) is therefore unchanged under time-reversal if
\[
f(r, k, s) = f^*(r, -k, -s).
\]

The complex conjugation \(^*\) arises from the fact that in quantum mechanics time-reversal is implemented by an antiunitary operator [20].

### 1.3 Time-Reversal Symmetry Breaking

Superconductivity does not need to break Time-Reversal symmetry, although some forms can. This can be either intrinsic to the superconducting state or due to extrinsic perturbations being imposed, for instance at the boundaries of the material [21]. The presence or absence of Time-Reversal symmetry breaking in a system cannot be determined by direct examination of the lattice structure, but must be inferred from careful analysis of the system’s behaviour.

The breaking of Time-Reversal symmetry may have been indicated in some ‘unconventional’ superconductors through the examination of a phenomena called the ‘Zero-Bias Conductance Peak’ (henceforth abbreviated to ZBCP). The ZBCP is observed in electron tunnelling experiments on some (though not all) ‘unconventional’ superconductors. We expect electron tunnelling between a non-superconducting lead and a superconductor to occur only at nonzero voltage differences (or ‘bias voltages’), as for a bias voltage of zero there should be no electronic states within the superconductor for the electrons to tunnel into. This is true for all conventional (and many unconventional) superconductors, but for some - Cuprates among them - a significant level of electron tunnelling occurs for a bias voltage of exactly zero, but not voltages around it [22–24]. This ‘peak’ in the electronic conductance at zero bias is what we call the ZBCP, and it is usually taken as evidence that these ‘unconventional’ superconductors possess exotic surface physics [25,26].

#### 1.3.1 ZBCP Splitting

Researchers studying high-temperature Cuprate superconductors have noted an unusual phenomena related to their Zero-Bias conductance peaks: Once the material is cooled below a certain temperature (distinct from and well below their known critical temperatures), the ZBCPs ‘split’ into two distinct peaks (see Fig. 1.2) [27–29]. This is generally seen as evidence that that a phase transition of some kind is taking place at this temperature. It has been proposed that this phase transition is the breaking of Time Reversal Symmetry, and there is experimental evidence to suggest that this is the case [30–32]. However, other experiments which are expected to be sensitive to Time-Reversal symmetry breaking (henceforth abbreviated to TRSB) have returned negative or ambiguous results [33–35].

Some researchers have proposed that the source of the TRSB - and thus the ZBCP splitting - in the Cuprate superconductors is the appearance of a second kind of Cooper pair, with a different angular momentum and lower critical temperature than the first [36–40]. The interaction between the two, they claim, makes the superconducting order parameters complex, causing TRSB. It should again be noted that there is not complete consensus among researchers on this point; while most hypothesize an additional Cooper pair, some posit the appearance of a magnetic order parameter [41–43]. One recent paper even claims that TRSB can be produced without a second order parameter of any kind [44]. Neverthe-
less, the concept of different coexisting kinds of superconductivity is compelling and could be realized in systems other than the cuprates.

1.3.2 Non-centrosymmetric Superconductors

A group of researchers led by C. Timm and P. Brydon were interested in taking the idea of multiple coexisting Cooper pairs even further. They were studying a family of materials known as ‘noncentrosymmetric’ superconductors, which have lattices that lack inversion symmetry. As stated previously, superconducting states can be classified by their behaviour under different symmetries: If two types of Cooper pair behave differently under the same symmetry, they are distinct and cannot readily coexist in the bulk.

The wavefunction for a singlet pair can be written

\[ \psi_s(r_1 - r_2)|0, 0\rangle \]  \hspace{1cm} (1.3)

while the wavefunction for a triplet pair is

\[ \sum_{m=-1}^{1} \psi_{t,m}(r_1 - r_2)|1, m\rangle \]  \hspace{1cm} (1.4)

where \( r_1 \) and \( r_2 \) are the position vectors of the constituent electrons. As these wavefunctions describe two fermions, they must be antisymmetric under the exchange of the particles. Thus as \(|0, 0\rangle\) is antisymmetric under particle exchange and \(|1, \pm 1\rangle\) and \(|1, 0\rangle\) are symmetric, \(\psi_s(r_1 - r_2)\) must be symmetric and \(\psi_{t,m}(r_1 - r_2)\) antisymmetric. As inversion takes \(k \rightarrow -k\) but leaves spin unaffected, the singlet state is even under inversion symmetry and the triplet state is odd. They are therefore fundamentally distinguished between by inversion symmetry and cannot readily coexist in its presence.

However, the loss of inversion symmetry complicates this picture. Theoretically, two forms of superconductivity that are normally distinct by virtue of their different behaviours under inversion symmetry but behave the same under the lattice’s other symmetries would be - in some sense - indistinguishable from each other under such circumstances. This could allow the system to support both states in the bulk simultaneously [45]. In physical terms, this suggests that Cooper pairs of different spin states (triplet and singlet)
can theoretically coexist in noncentrosymmetric superconductors. This remarkable conjecture is backed up by significant evidence of unconventional behaviour by a number of noncentrosymmetric superconductors including CePt$_3$Si [46], Li$_2$(Pd$_{1-x}$Pt$_x$)$_3$B [47], and CeIrSi$_3$ [48].

If (and only if) the spin-triplet pairing is dominant, these and other noncentrosymmetric superconductors have been predicted to develop similar surface states to the Cuprates, including a ZBCP and hence also ZBCP splitting [49–52]. This raises the question of whether or not similar TRSB states can occur in these materials. It is this conjecture that these researchers sought to evaluate. Using a computational model based on a modified version of the BCS theory, Timm et al. concluded that TRSB would indeed take place, with an interesting feature: They calculated that the phase difference between the two order parameters would be nonzero at the surface, but die away to zero in the bulk over a distance far greater than that which it took for the absolute values of the parameters to revert to their (nonzero) bulk values [53]. In Time-Reversal Symmetry terms, TRS would be broken only at and around the surface, not in the bulk. The modified BCS program’s output is displayed in Fig. 1.3.

![Figure 1.3: Plot by Timm et al. displaying the microscopic modified BCS predicted behaviour of the two order parameters near the border. They have taken the material’s boundary to be the (1 0 1) surface. $\Delta^s_l$ is a spin-singlet order parameter that measures the concentration of s-wave Cooper pairs, while $\Delta^{x+1/2}_l$ and $\Delta^y_l$ denote the x and y components of a spin-triplet order parameter that measures the concentration of p-wave Cooper pairs. In theory these two components could behave very differently, but here they are very closely correlated. Here l is used to denote lattice sites rather than angular momentum. Reproduced with permission.](image)

### 1.3.3 Thesis Motivation

Unfortunately the model created by Timm et al. takes weeks to run, making it impractical for determining the true physical viability of the state they had described. This thesis
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aims to construct a much-faster phenomenological model, explicitly connect it to the microscopic case, and use this model to evaluate the viability of the system described in their paper.

Chapter 2 elucidates some necessary techniques from quantum many-particle theory. Chapter 3 details a mean-field treatment of a microscopic superconducting Bogoliubov Hamiltonian, while Chapter 4 introduces the macroscopic Ginzburg-Landau free energy and shows how it can be used to obtain the behaviour of complex systems. Chapters 5 and 6 outline the use of a Linked Cluster Expansion to connect the macroscopic to the microscopic, and Chapter 7 completes this process and uses a microscopically-derived Ginzburg-Landau free energy to describe the TRSB availability of both centrosymmetric and non-centrosymmetric systems. Finally, Chapter 8 presents the conclusions we may come to as a result of this work.
Many-Particle Quantum Systems

In the previous chapter, we were introduced to the essential features of superconductivity and learned of the first successful microscopic attempt to explain them: The BCS theory. We also learned that there are unconventional superconductors that diverge from the expected behaviour and physical traits of traditional BCS superconductors, and that the study of one such divergence - ZBCP splitting - gave rise to a bold prediction from Timm et al.: certain non-centrosymmetric systems can sustain triplet and singlet Cooper pairs simultaneously, and when the triplet pair is suppressed near the surface TRSB results but disappears in the bulk.

We will be examining this claim in detail, but doing so requires a certain familiarity with concepts from the quantum theory of many-particle systems. In this chapter we will introduce and describe Matsubara electron Green’s functions, time-ordering, and Wick’s theorem. Readers familiar the above may safely skip this chapter. The following is drawn largely from Mahan [54] and Fetter & Walecka [55].

2.1 The Interaction Representation

There are three basic representations of quantum mechanics, the first of which is the Schrödinger representation. In Schrödinger representation, a wave function $|\Psi(t)\rangle$ has time dependence (taking $\hbar \to 1$):

$$|\Psi_S(t)\rangle = e^{-iHt}|\Psi(0)\rangle$$  \hspace{1cm} (2.1)

where $H$ is the system’s Hamiltonian. $H$, and all other operators, are taken to be independent of time in this representation. This is not the case in the Heisenberg representation, in which the wave functions are taken to be independent of time and operators are taken to have a time dependence

$$A_H(t) = e^{iHt}A(0)e^{-iHt}.$$ \hspace{1cm} (2.2)

Note that these two representations both give the same result for the expectation value of $A$:

$$\langle \Psi_S(t)\vert A(0)\vert \Psi_S(t)\rangle = \langle \Psi(0)\vert e^{iHt}A(0)e^{-iHt}\vert \Psi(0)\rangle = \langle \Psi(0)\vert A_H(t)\vert \Psi(0)\rangle .$$ \hspace{1cm} (2.3)

This is the case for all observable results in all representations, including the interaction representation, which is the one we will be using in this thesis. In the interaction representation, the Hamiltonian is split into two parts

$$H = H_0 + V_0$$ \hspace{1cm} (2.4)
where \( H_0 \) describes the free motion of the individual particles, and \( V_0 \) describes the interaction between them. Both operators and wave-functions have a time dependence in this representation:

\[
A_I(t) = e^{iH_0t}A(0)e^{-iH_0t}
\]  
(2.5)

and

\[
|\Psi_I(t)\rangle = e^{iH_0t}e^{-iHt}|\Psi(0)\rangle.
\]  
(2.6)

### 2.2 Matsubara Green’s Functions

The Matsubara method introduces the real quantity \( \tau = it \),

which implies that the time \( t \) is now imaginary. Under this regime the interaction-picture \( \tau \)-dependencies of wave-functions and operators are

\[
|\Psi(\tau)\rangle = e^{H\tau}e^{-H\tau}|\Psi(0)\rangle
\]  
(2.7)

and

\[
A(\tau) = e^{H\tau}A(0)e^{-H\tau}.
\]  
(2.8)

We define the electron Green’s functions themselves as

\[
G(k, \tau - \tau') = \langle T_\tau C_{k\sigma}(\tau) C_{k\sigma}^\dagger(\tau') \rangle,
\]  
(2.9)

where \( C^\dagger \) and \( C \) are the electron creation and annihilation operators for momentum eigenstate \( k \) and spin \( \sigma \) and \( T_\tau \) is the time-ordering operator in \( \tau \):

\[
T_\tau C_{k\sigma}(\tau) C_{k\sigma}^\dagger(\tau') = \begin{cases} 
C_{k\sigma}(\tau) C_{k\sigma}^\dagger(\tau') & \tau > \tau' \\
-C_{k\sigma}^\dagger(\tau') C_{k\sigma}(\tau) & \tau' > \tau,
\end{cases}
\]

where the \( - \) sign in the second case arises from the anticommutation of the two fermionic operators. \( T_\tau \) can act on groups of operators of any size, and arranges them from highest to lowest in \( \tau \) by a series of commutations or anticommutations, depending on whether the operators are bosonic or fermionic. The \( \langle \cdots \rangle \) represents the taking of an ‘ensemble average’:

\[
\langle \cdots \rangle = \frac{1}{Z} \text{Tr} \left\{ \cdots e^{-\beta(H-\mu N)} \right\},
\]  
(2.10)

where \( Z \) is the grand canonical ensemble partition function:

\[
Z = \text{Tr} \left\{ e^{-\beta(H-\mu N)} \right\}
\]  
(2.11)

in which \( \mu \) is the chemical potential, \( N \) is the particle-number operator, \( \beta \) is the ‘inverse temperature’

\[
\beta = \frac{1}{k_BT},
\]  
(2.12)

and where \( \text{Tr} \) denotes the ‘trace’ of the system, a sum over a complete set of orthonormal states \( |\eta\rangle \):

\[
\text{Tr}\{\cdots\} = \sum_{\eta} \langle \eta | \cdots | \eta \rangle.
\]  
(2.13)
In practice $-\mu N$ is usually absorbed into $H_0$, changing $H_0 \rightarrow H_0 - \mu N$ in the time-dependence of the operators.

So-called ‘non-interacting’ Green’s functions are the Green’s functions for the $H_0$ of the system only, and are given by

$$G^{(0)}(k, \tau - \tau') = \langle T_\tau C_k \sigma(\tau) C_k^\dagger \sigma(\tau') \rangle. \quad (2.14)$$

While $\langle \cdots \rangle$ is a trace over the true eigenstates of the system, $\langle_0 \langle \cdots \rangle$ is a trace over the eigenstates of $H_0$ only:

$$\langle_0 \langle \cdots \rangle = \frac{1}{Z_0} \text{Tr} \left\{ \cdots e^{-\beta(H_0-\mu N)} \right\}, \quad (2.15)$$

where $Z_0$ is the partition function of the non-interacting system:

$$Z_0 = \text{Tr} \left\{ e^{-\beta(H_0-\mu N)} \right\}. \quad (2.16)$$

Matsubara Green’s functions are functions of $\tau$ with domain

$$-\beta \leq \tau \leq \beta,$$

meaning that they have the Fourier transform properties

$$G(k, i\omega_n) = \int_0^\beta d\tau e^{i\omega_n \tau} G(k, \tau) \quad (2.17)$$

and

$$G(k, \tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} e^{-i\omega_n \tau} G(k, i\omega_n), \quad (2.18)$$

where

$$\omega_n = \begin{cases} \frac{2\pi n}{\beta} & \text{for Bosons} \\ \frac{(2n+1)\pi}{\beta} & \text{for Fermions.} \end{cases} \quad (2.19)$$

The frequency form of the non-interacting Green’s function is of particular interest; $G^{(0)}$ has time dependence

$$-e^{\xi_k - k\tau} [\Phi(\tau) - n_F(\xi_k)] \quad (2.20)$$

where $n_F$ is the expectation value of the number operator, which has the form

$$n_F = \frac{1}{e^{\beta \xi_k} + 1} \quad (2.21)$$

and

$$\xi_k = \varepsilon_k - \mu \quad (2.22)$$

where $\Phi$ is the Heaviside function, $\mu$ is the system’s chemical potential, and $\varepsilon_k$ is the energy of a single particle in state $k$. This means that $G^{(0)}(k, i\omega_n)$ can be written

$$G^{(0)}(k, i\omega_n) = \int_0^\beta d\tau e^{i\omega_n \tau} G^{(0)}(k, \tau) = \frac{1}{i\omega_n - \xi_k}, \quad (2.23)$$

which is a gratifyingly simple expression to deal with. This formulation will be of great use to us in future.

We now know the definition of Matsubara electron Green’s functions, but how are we
to deal with them in the wild? How, for example, would we express
\[ 0 \langle T_\tau C_k(\tau_1)C_{k'}^\dagger(\tau_2)C_{k''}(\tau_3)C_{k'''}^\dagger(\tau_4) \rangle \] (2.24)
in terms of Green’s functions? Luckily, there is a theorem for exactly this occasion.

2.2.1 Wick’s Theorem

Wick’s theorem states that in evaluating a trace, time-ordering each possible pair of operators will correctly time-order the whole result. Thus for arbitrary operators \( A, B, C, D, E \... \)
\[ \langle T_\tau ABCDE... \rangle = \langle T_\tau AB \rangle \langle T_\tau CD \rangle... \mp \langle T_\tau AC \rangle \langle T_\tau BD \rangle... \pm \langle T_\tau AD \rangle \langle T_\tau BC \rangle... + ... \] (2.25)
where the top sign is for fermionic operators and the bottom for bosonic. The application of Wick’s theorem is rather simplified in the case of eq. 2.24 by the fact that taking the trace of an unequal number of creation and annihilation operators over \( H_0 \) gives zero - we therefore only have to concern ourselves with creation-annihilation pairs. Taking all non-zero operator pairings, eq. 2.24 can be written
\begin{align*}
0 \langle T_\tau C_k(\tau_1)C_{k'}^\dagger(\tau_2)\rangle & - 0 \langle T_\tau C_k(\tau_1)C_{k''}^\dagger(\tau_3)\rangle
- \delta_{kk''} \delta_{k'k'''} \langle T_\tau C_k(\tau_1)C_{k'}^\dagger(\tau_2)\rangle \langle T_\tau C_{k''}(\tau_3)C_{k'''}^\dagger(\tau_4)\rangle,
\end{align*}
(2.27)
or
\begin{align*}
\delta_{kk'} \delta_{k''k'''} & \langle T_\tau C_k(\tau_1)C_{k'}^\dagger(\tau_2)\rangle \langle T_\tau C_{k''}(\tau_3)C_{k'''}^\dagger(\tau_4)\rangle
- \delta_{kk''} \delta_{k'k'''} \langle T_\tau C_k(\tau_1)C_{k'}^\dagger(\tau_2)\rangle \langle T_\tau C_{k''}(\tau_3)C_{k'''}^\dagger(\tau_4)\rangle,
\end{align*}
(2.28)
as within a pairing bracket, the subscripts \( k, k' \) must be the same as they denote eigenstates. Note that the second pair of pairings is negative, as an odd number of anticommutations have occurred arranging the operators into the correct order.

Thus using Wick’s theorem, eq. 2.24 can be written
\[ \delta_{kk'} \delta_{k''k'''} G^{(0)}(k, \tau_1 - \tau_2) G^{(0)}(k', \tau_3 - \tau_4) - \delta_{kk''} \delta_{k'k'''} G^{(0)}(k, \tau_1 - \tau_4) G^{(0)}(k', \tau_3 - \tau_2) \] (2.29)
and we observe that for \( n \) each creation and annihilation operators, Wick’s Theorem gives \( n! \) possible pairings. Having learned of the interaction representation, Matsubara electron Green’s functions, \( \tau \)-ordering and Wick’s theorem, we are now equipped to embark on our examination.
Chapter 3

The Bogoliubov Hamiltonian

In the previous chapter, we reviewed basic theoretical tools for the study of many-particle systems, including time ordering, imaginary time, Matsubara electron Green’s functions, and Wick’s theorem. We will now be beginning our investigations in earnest, and outlining the rudiments of the mean-field theory of superconductivity and the grand canonical ensemble.

For our inquiries to have any validity, they should be grounded in the most accurate theories we have. We will therefore start with a spatially-homogeneous singlet $s$-wave system, which can be solved analytically with far less effort than more complex systems.

3.1 The Mean-Field Approximation

The standard electron Hamiltonian is given by

$$H = \sum_{k\sigma} \xi_k C_{k\sigma}^\dagger C_{k\sigma} - \frac{V}{N} \sum_{k,k'} C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger C_{-k'\downarrow} C_{k'\uparrow},$$ (3.1)

where $V$ is the two-particle interaction potential, which we treat as a constant and which in the BCS theory arises from the electron-phonon coupling described in Chapter 1, and where $N$ is the number of grid points in our $k$-space mesh [54]. We can rewrite this as

$$H = \hat{H}_0 + \hat{V}_0,$$

with

$$\hat{H}_0 = \sum_{k\sigma} \xi_k C_{k\sigma}^\dagger C_{k\sigma},$$ (3.2)

and

$$\hat{V}_0 = -\frac{V}{N} \sum_{k,k'} C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger C_{-k'\downarrow} C_{k'\uparrow}.$$ (3.3)

We now perform a mean-field decoupling of the $\hat{V}$ term, treating it as an ensemble average perturbed by a very small fluctuation $\delta$:

$$C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger = \langle C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger \rangle + \delta C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger,$$ (3.4)

giving

$$\hat{V}_0 = -\frac{N}{V} |\Delta|^2 - \sum_{k,k'} \frac{V}{N} (\delta C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger) (\delta C_{-k'\downarrow} C_{k'\uparrow}) + \sum_k \delta C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger \Delta + \sum_{k'} \delta C_{-k'\downarrow} C_{k'\uparrow} \Delta^\dagger,$$
where we have defined
\[ \Delta = -\frac{V}{N} \sum_k \langle C_{-k\downarrow} C_{k\uparrow} \rangle. \] (3.5)

the operators within \( \Delta \) represent the creation of a Cooper pair - annihilating two opposite-spin electrons in the process (similarly the operators within \( \Delta^\dagger \) represent the annihilation of a Cooper pair, creating two such electrons). The ensemble average \( \Delta \) is thus a pairing potential that can be taken as a measure of the concentration of Cooper pairs within the system, and is called the 'order parameter'. This is an important result, and we will be returning to it.

We assume that the correlation between fluctuations in negligible, allowing us to neglect the \( \delta\delta \) term and leaving us with
\[ \hat{V}_0 \approx -\frac{N}{V} |\Delta|^2 + \sum_k \delta C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} \Delta + \delta C_{-k\downarrow} C_{k\uparrow} \Delta^\dagger. \] (3.6)

yielding the mean-field approximation of \( \hat{V}_0 \)
\[ \hat{V}_0 \approx \frac{N}{V} |\Delta|^2 + \sum_k +\Delta C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} + \Delta^\dagger C_{-k\downarrow} C_{k\uparrow}. \] (3.7)

allowing us to write the Hamiltonian as
\[ H = \hat{H}_0 + \frac{N}{V} |\Delta|^2 + \hat{V}, \] (3.8)

where
\[ \hat{V} = \sum_k \Delta C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} + \Delta^\dagger C_{-k\downarrow} C_{k\uparrow}. \] (3.9)

This formulation is called the Bogoliubov Hamiltonian, and will be useful to us. If necessary the fluctuation \( \delta \) can be taken to vary in space and/or time, but doing so is rather complex and will not be necessary in the course of this thesis.

### 3.2 The Grand Canonical Ensemble

The Bogoliubov Hamiltonian allows us to apply the grand canonical ensemble (GCE) to calculate the free energy and critical temperature of our simple superconductor. The GCE ‘Grand potential’ \( \Omega \) is given by
\[ \Omega = -\frac{1}{\beta} \log(Z), \] (3.10)

but for this system of electrons \( Z \) can be written
\[ Z = \sum_j e^{-\beta(E_j - \mu N_j)}. \] (3.11)

where \( E_j \) and \( N_j \) are the energy and occupation number of state \( j \), respectively.
We can represent eq. 3.8 as
\[
\sum_k \left( C_{k\uparrow} \ C_{-k\downarrow} \right) \left( \xi_k \Delta \ \ -\xi_k \right) \left( C_{k\uparrow} \ C_{-k\downarrow} \right) + \frac{N}{V} |\Delta|^2,
\] (3.12)
and diagonalising the Hamiltonian shows there are only two energies possible, which we will label $\tilde{E}_\pm$:
\[
\tilde{E}_\pm = \pm E_k + \frac{N|\Delta|^2}{V},
\] (3.13)
where
\[
E_k = \sqrt{\xi_k^2 + |\Delta|^2}.
\] (3.14)
Note that if $\Delta = 0$, $\tilde{E}_\pm = \pm \xi_k$ and we recover normal state dispersion. The presence of the order parameter (and thus superconductivity), opens an energy gap between the $\tilde{E}_+$ and $\tilde{E}_-$ parts of the Fermi surface [54]. We can now write the partition function $Z$ as
\[
Z = e^{-\beta \frac{N|\Delta|^2}{V}} \prod_{k, \pm} \left( 1 + e^{-\beta (\pm E_k)} \right)
\] (3.15)
(recalling that for fermions, the occupation number is 0 or 1). Plugging this into the $\Omega$ expression gives
\[
\Omega = \frac{N|\Delta|^2}{V} - \sum_k E_k + \frac{2}{\beta} \log \left( 1 + e^{-\beta E_k} \right).
\] (3.16)
We can now manipulate this into a form that allows us to calculate the critical temperature of our system. We start by differentiating $\Omega$ with regard to $\Delta$:
\[
\frac{\partial \Omega}{\partial \Delta} = \frac{N \Delta}{V} - \sum_k \frac{\Delta}{2E_k} - \frac{\Delta e^{-\beta E_k}}{E_k(1 + e^{-\beta E_k})}
\] (3.17)
(recalling that $E_k = \sqrt{|\Delta|^2 + \xi_k^2}$). At $T_c$, we may naively expect
\[
\frac{\partial \Omega}{\partial \Delta} = 0,
\]
but there’s a problem: as this has the form of
\[
\frac{\partial \Omega}{\partial \Delta} = \Delta \mathcal{F}(\Delta, T),
\]
$\Delta = 0$ will always be a solution. However, dividing by $\Delta$ allows us to write the condition
\[
\mathcal{F}(T) = \frac{N}{V} - \sum_k \frac{1}{2\xi_k} - \frac{1}{\xi_k(1 + e^{\beta \xi_k})}
\] (3.18)
which will be zero at $T_c$, negative below $T_c$, and positive above $T_c$, making it a far more useful quantity to examine. We now need some way to evaluate the sum over $k$. In this thesis, we will be using the two dimensional tight-binding approximation. In this approximation
\[
\xi_k = -2t \left[ \cos(k_x a) + \cos(k_y a) \right],
\] (3.19)
where $a$ is the lattice constant, $t$ is the ‘hopping integral’, and $k_x$ and $k_y$ are evaluated
The Bogoliubov Hamiltonian

separately from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ at $\sqrt{N}$ points, giving $N$ sites in all [56]. For the rest of this thesis, we will be using the energy scale defined by $2t = 1$. In order to make things as general as possible, we will be dealing with the free energy ‘per-particle’, necessitating the division of eq. 3.20 by $N$. Thus what we actually evaluate is

$$F(T) = \frac{1}{V} - \frac{1}{N} \sum_k \frac{1}{2\xi_k} - \frac{1}{\xi_k(1 + e^{\beta\xi_k})}. \quad (3.20)$$

Doing this gives Fig. 3.1, which shows that the critical temperature for the system we’re considering is approximately $k_B T/(2t) = 0.001$. This indicates that our choice for $t$ is reasonably sound - in physical systems the critical temperature is orders of magnitude smaller than the Fermi temperature, which is defined by

$$T_F = \frac{\epsilon_F}{k_B} \quad (3.21)$$

for Fermi energy $\epsilon_F$. Our $T_c$ of 0.001 gives $T_c << T_F$, as required. The choice of $t$ also sets the bandwidth, which in physical systems is also several orders of magnitude greater than $k_B T_c$ - again, a condition satisfied by our choice. As we deal only with $k_B T$ in this thesis, we have effectively set $k_B = 1$ throughout.

We can additionally calculate the value of $\Delta$ for our system by computationally minimising eq. 3.16 in MATLAB. This gives us Fig. 3.2, which shows that below the $T_c \Delta$ steadily rises until the system reaches saturation at approximately $0.25T_c$.

![Graph](image)

Figure 3.1: GCE condition vs $k_B T$ for $N = 2000^2, V = 0.4$, and $\mu = 0.3$. $k_B T$ is in units of $2t$. A line at 0 on the y-axis has been added to enable the discernment of $T_c$. The GCE condition is dimensionless.
3.3 Inversion Symmetry Breaking

Given our success so far, it seems natural to go on to apply these techniques to the more complex non-centrosymmetric case. The breaking of inversion symmetry implies the normal state Hamiltonian is not symmetric in $k$ (see eq. 1.1), eg.

$$H_0(-k) \neq H_0(k), \quad (3.22)$$

but we will assume that Time-Reversal Symmetry is not broken, which means that

$$(i\hat{\sigma}_y) H_0^*(-k)(-i\hat{\sigma}_y) = H_0(k), \quad (3.23)$$

where $\hat{\sigma}_y$ is the $y$ Pauli matrix (see eq. 1.2). This allows additional terms to occur within the normal state Hamiltonian describing ‘antisymmetric spin-orbit coupling’, an interaction between the spin of an electron and the effective magnetic field that it experiences in its rest frame [57]. These terms are of the form

$$H_0(k) \rightarrow \xi_k \hat{\sigma}_0 + \lambda \vec{g}_k \cdot \vec{\sigma} \quad (3.24)$$

where $\vec{g}_{-k} = -\vec{g}_k$ (hence the ‘antisymmetric’ part of antisymmetric spin-orbit coupling) and $\vec{\sigma}$ is the set of Pauli matrices. The form of $\vec{g}_k$ is determined by the crystal symmetries of the system; an exhaustive list has been compiled by Samokhin [58]. We will be focusing on a form of spin-orbit coupling called ‘Rashba spin orbit coupling’ after its discoverer, in

![GCE Δ values vs Temp](image.png)

Figure 3.2: Predicted $\Delta$ values vs $k_B T$ for $N = 2000^2, V = 0.4$, and $\mu = 0.3$. $k_B T$ and $\Delta$ are in units of $2t$. 
is a special triplet state that displays only inter- or intra-band. Inter-band pairings are usually energetically unfavourable, but there are tight restraints placed on the pairings \[45\]. Singlet pairings can only occur anti-parallel to \(\vec{g}_k\) and spin singlet Cooper pairs (and thus order parameters \(\Delta_t\) and \(\Delta_s\)) to coexist \[57\]. However, there are tight restraints placed on the pairings \[45\]. Singlet pairings can only occur between electrons in the same helical band, while the triplet pairings can theoretically be inter- or intra-band. Inter-band pairings are usually energetically unfavourable, but there is a special triplet state that displays only intra-band paring which is given by

\[
\sum_{i,j} C_{ki}^\dagger [(\vec{g}_k \cdot \vec{\sigma})(i\sigma_y)]_{ij} C_{-kj}^\dagger
\]  

(3.27)

for spin indices \(i, j\) \[45\]. We can incorporate this into the Bogoliubov Hamiltonian by taking

\[
\hat{V}_0 = -\frac{V_t}{N} \sum_{k,k'} C_{k\uparrow}^\dagger C_{-k\downarrow} - C_{k\downarrow}^\dagger C_{-k\uparrow} (C_{-k'\uparrow} C_{k'\downarrow} - C_{-k'\downarrow} C_{k'\uparrow}) \\
- \frac{V_s}{N} \sum_{k,k'} \left( \sum_{i,j} C_{ki}^\dagger [(\vec{g}_k \cdot \vec{\sigma})(i\sigma_y)]_{ij} C_{-kj}^\dagger \right) \left( \sum_{i',j'} C_{k'i'}^\dagger [(\vec{g}_k \cdot \vec{\sigma})(i\sigma_y)]_{i'j'} C_{-k'j'} \right)
\]

(3.28)

where \(V_t\) and \(V_s\) are the interaction potentials for the triplet and singlet states respectively. Note that because \(C_{k\uparrow}^\dagger C_{-k\downarrow} - C_{k\downarrow}^\dagger C_{-k\uparrow}\) as \(k \rightarrow -k\) we have had to divide by 2 to avoid double-counting of \(k\)-states. Applying the mean-field decoupling to this gives

\[
H = \hat{H}_0 + \frac{N}{V_s} |\Delta_s|^2 + \frac{N}{V_t} |\Delta_t|^2 + \hat{V},
\]

(3.29)

where

\[
\Delta_s = \frac{1}{2} \frac{V_s}{N} \sum_k \left( \langle C_{-k\downarrow} C_{k\uparrow} \rangle + \langle C_{-k\uparrow} C_{k\downarrow} \rangle \right),
\]

(3.30)

\[
\Delta_t = \frac{1}{2} \frac{V_t}{N} \sum_k \left( \langle l_k^* C_{-k\uparrow} C_{k\uparrow} \rangle - \langle l_k C_{-k\downarrow} C_{k\downarrow} \rangle \right),
\]

(3.31)

and

\[
\hat{V} = \frac{1}{2} \sum_k \left[ \Delta_s \left( C_{k\uparrow}^\dagger C_{-k\downarrow} - C_{k\downarrow}^\dagger C_{-k\uparrow} \right) + \Delta_s^* \left( C_{-k\uparrow} C_{k\downarrow} - C_{-k\downarrow} C_{k\uparrow} \right) \\
+ \Delta_t \left( l_k C_{k\uparrow}^\dagger C_{-k\downarrow} - l_k^* C_{k\downarrow}^\dagger C_{-k\uparrow} \right) + \Delta_t^* \left( l_k^* C_{-k\uparrow} C_{k\downarrow} - l_k C_{-k\downarrow} C_{k\uparrow} \right) \right]
\]

(3.32)
for the symmetry factor
\[ l_k = \sin(k_y a) - i \sin(k_x a) . \quad (3.33) \]

Following the approach of eq. 3.12, we can now write
\[
H = \sum_k \left( C_{k+}^\dagger \begin{bmatrix} C_{k+}^\dagger & C_{-k-} & C_{-k+} & C_{k-} \end{bmatrix} \right) \begin{pmatrix} \xi_k & \lambda l_k & l_k \Delta_t & -\Delta_s \\ \lambda l_k^* & \xi_k & -\Delta_s & \lambda l_k \\ -\Delta_s^* & -l_k \Delta_t & \lambda l_k^* & -\xi_k \\ \Delta_s^* & l_k \Delta_t^* & -\xi_k & \lambda l_k^* \end{pmatrix} \begin{pmatrix} C_{k+} \\ C_{k-}^\dagger \\ C_{-k+}^\dagger \\ C_{-k-}^\dagger \end{pmatrix} (3.34)
\]
\[
+ \frac{N}{V_s} |\Delta_s|^2 + \frac{N}{V_t} |\Delta_t|^2 .
\]

This looks very complicated indeed, but because we are dealing only with intra-band coupling we can simplify it expression by applying a transformation to take us from the spin basis to the helicity basis [60]:
\[
\begin{pmatrix} C_{k+}^\dagger \\ C_{k-} \end{pmatrix} = \begin{pmatrix} u_{k+} & v_{k+} \\ -v_{k-}^* & u_{k-}^* \end{pmatrix} \begin{pmatrix} C_{k+}^\dagger \\ C_{k-} \end{pmatrix}
\]
\[
\text{the hermitian conjugate also applies},
\]
\[
u_{k+} = \frac{1}{\sqrt{2} |l_k|} \left[ \sin (k_y a) - i \sin (k_x a) \right] .
\]

The Hamiltonian can now be written
\[
H \rightarrow \tilde{H} = \sum_k \left( C_{k+,+}^\dagger C_{k,-}^\dagger C_{-k,-} C_{-k,+} \right) \begin{pmatrix} \xi_k^+ & 0 & \Delta_+ & 0 \\ 0 & \xi_k^- & 0 & \Delta_- \\ \Delta_+^* & 0 & -\xi_k^- & 0 \\ 0 & \Delta_-^* & 0 & -\xi_k^+ \end{pmatrix} \begin{pmatrix} C_{k,+} \\ C_{k,-} \\ C_{-k,+}^\dagger \\ C_{-k,-}^\dagger \end{pmatrix} (3.37)
\]
\[
+ \frac{N}{V_s} |\Delta_s|^2 + \frac{N}{V_t} |\Delta_t|^2 .
\]

This transformation will be explored further in Chapters 5 and 6. Our new \( \tilde{H} \) looks like it describes two separate, uncoupled superconductors similar to the one described by eq. 3.12 - one for \( \Delta_+ , \xi_k^+ \) and one for \( \Delta_- , \xi_k^- \). In principle it is possible to extend this line of thinking and write the free energy as
\[
\Omega = \frac{N|\Delta_s|^2}{V_s} + \frac{N|\Delta_t|^2}{V_t} - \frac{1}{2} \sum_{k,\pm} \frac{1}{\beta} \left[ \log \left( 1 + e^{-\beta E_{k,\pm}} \right) + \log \left( 1 + e^{\beta E_{k,\pm}} \right) \right] (3.38)
\]
for the \( \pm \) excitation spectrum \( E_{k,\pm} \), but this is deceptively difficult to obtain any results
from as $\Delta_s$ and $\Delta_t$ are still connected by the dispersion $E_{k,\pm}$.

There is another issue with using this approach: We have been assuming so far that we are dealing with an infinite, homogeneous system so that $k$ is a useful quantum number, but this assumption fails in the presence of inhomogeneities such as a vortex core or the edge of the superconducting material. Given that we are particularly interested in examining the area near the edge of our system, this is a serious defect. It is possible to modify the mean-field theory approach to accommodate inhomogeneities as Timm et al. did, but this quickly becomes very technically and computationally demanding. To incorporate spatial variation in even the relatively simple $s$-wave singlet system dealt with earlier at $L$ sites would require us to diagonalize a $2L \times 2L$ matrix to determine the free energy for the set of order parameters - but this means we will also have to deal with $2L$ variational mean fields (representing $\Delta$ and $\Delta^*$ at each lattice point) and for any physically-useful value of $L$ this is a daunting problem.

This rapid scaling of complexity makes using the techniques outlined in this chapter impractical going forward. Luckily, there is a relatively simple theory that allows us to deal with complex systems in a straightforward, more easily scaled way: The Ginzburg-Landau Theory.
Chapter 4

The Ginzburg-Landau Theory

In the previous chapter, we examined the Bogoliubov Hamiltonian for a very simple superconducting system. This allowed us to predict the critical temperature of the system, as well as the behaviour of $\Delta$ below $T_c$. We also acknowledged that the mean-field theory approach used to obtain such results would rapidly scale in complexity as we proceeded to more complicated cases. In this chapter we will learn of a useful alternative: The Ginzburg-Landau Theory.

4.1 The Ginzburg-Landau Free Energy

In 1950, seven years prior to Bardeen, Cooper, and Schrieffer’s triumph, two Russian physicists - Lev Landau and Vitaly Ginzburg - produced an immensely useful phenomenological theory of superconductivity. While Ginzburg and Landau lacked the framework to understand why superconductivity occurred, they could still describe it at a macroscopic level. They argued that the local density of superconducting charge carriers could be modelled by a complex superconducting order parameter $\Delta(r)$. This order parameter essentially measures the extent to which the system is ordered in a superconducting state at position $r$, and it is now known to be equivalent to the homogeneous order parameter $\Delta$ defined in the previous chapter. They claimed that the free energy $F$ could be represented as a functional of the order parameter and the magnetic potential $A(r)$ [1]:

$$F = \int f[\Delta(r), A(r)] d^3r,$$

where $f$ is a quantity that is integrated over all space to obtain the free energy. For this reason, we call it the free energy density. Provided $\Delta(r)$ is ‘small’ and varies slowly in space, Ginzburg and Landau proposed the following form:

$$f[\Delta(r), A(r)] = f_n + \alpha |\Delta(r)|^2 + \beta |\Delta(r)|^4 + \frac{1}{2m^*} \left( \frac{\hbar^2}{m^*} |\Delta(r)|^2 + \frac{B^2}{8\pi} \right)^2$$

where $f_n$ is the free energy density of the non-superconducting state, $A$ and $B$ are the magnetic vector potential and field as usual, $e^*$ and $m^*$ are the charge and mass of the superconducting charge carriers, and $\alpha$ and $\beta$ are real constants.

This theory was constructed before Cooper demonstrated that paired electrons are what carry charge in superconductors, so we now know that $e^*$ is simply $2e$. $m^*$ is usually $2m_e$, but in some materials - such as the Heavy Fermion family of superconductors - it has been measured as being much larger. We therefore treat it as a free parameter.
Our treatment of this free energy density will be significantly simplified by the temporary assumption that there is no magnetic potential present within the material in question (i.e. $A = B = 0$). This results in the much more manageable expression

$$f[\Delta(r)] = f_n + \alpha|\Delta(r)|^2 + \beta|\Delta(r)|^4 + \frac{\hbar^2}{2m^*}(|\nabla\Delta(r)|^2).$$  \hspace{1cm} (4.3)

The first three terms are reasonably straightforward: $f_n$ is a constant, the $\alpha$ term is a quadratic, the $\beta$ term a quartic. The last term imposes a free-energy cost on any nonzero $\Delta$ gradient, preventing rapid spatial changes in its magnitude. To gain a better understanding of this system, let us take the case of the ‘bulk’: Deep inside the superconductor where $\Delta(r)$ will have reached spatial uniformity. Here the gradient term will be zero, leaving our free energy a combination of a constant, a quadratic, and a quartic. If $\beta$ is negative, then the free energy is unbounded and can go to $-\infty$ as $\Delta \to \infty$. This is plainly unphysical, so $\beta$ must be positive.

![Free Energy vs $\Delta$ for positive $\alpha$](image1)

![Free Energy vs $\Delta$ for negative $\alpha$](image2)

Figure 4.1: A comparison of negative and positive $\alpha$ for positive $\beta$ and $f_n = 0$, with minima marked: for $\alpha > 0$ the free energy is minimized by $\Delta = 0$ and so the system does not describe a superconductor; for $\alpha < 0$ the free energy is minimized by $\Delta = \pm \Delta_{\text{bulk}}$ (see below), implying a superconducting state. This plot is schematic and unit-agnostic.

Thus, as Fig. 4.1 demonstrates, in order for our system to superconduct $\alpha$ must be negative and $\beta$ positive: If $\alpha$ is positive $\Delta = 0$ minimises the system’s free energy and the material does not superconduct - this is the system’s ‘normal state’. It can therefore be said that non-superconducting systems are characterised by a positive $\alpha$. A system with negative $\alpha$ and positive $\beta$ reaches a minimum at

$$\Delta = \sqrt{ \frac{|\alpha|}{2\beta} } = \Delta_{\text{bulk}}$$ \hspace{1cm} (4.4)$$

which is the ‘bulk value’ of the system: the value that $\Delta$ will assume in the bulk of the material.

We have now established that a superconducting system must have a negative $\alpha$. For this reason, it is natural to introduce a phenomenological temperature dependence:

$$\alpha = \alpha_0(T - T_c),$$  \hspace{1cm} (4.5)

for some positive constant $\alpha_0$ and the critical temperature of the material $T_c$. Thus when
The system is cooled below the critical temperature, $\alpha$ becomes negative and the system becomes superconducting. Note that as $\Delta_{\text{bulk}}$ is proportional to $\sqrt{|\alpha|}$, this expression for $\alpha$ results in the prediction that below $T_c$

$$\Delta_{\text{bulk}} \propto \sqrt{T_c - T}. \quad (4.6)$$

This is precisely what the BCS theory and other mean-field models predict - in fact this relationship between the order parameter and $\sqrt{T_c - T}$ is a hallmark of mean-field theories [61].

Tinkham calls the Ginzburg-Landau (henceforth abbreviated to G-L) theory a ‘triumph of physical intuition’, and it is not difficult to see why. This ‘intuition’ was vindicated in spectacular fashion in 1959 when Lev Gor’kov proved that it could be derived from a rigorously limited case of the microscopic mean-field theory near $T_c$ [62]. Since then, it has been utilised widely as a powerful modelling tool accessible to newcomers as well as veteran superconductor researchers. Ease-of-use is not the G-L theory’s only advantage, however: It can allow us to understand inhomogeneous systems, such as near surfaces or vortex cores, which as we have found are extremely complex and difficult (some prohibitively so) to deal with using the microscopic approach.

### 4.1.1 Boundary Suppression

One such system is the area around the boundary of a superconductor. In ‘unconventional’ superconductors, the unusual $l > 0$ pairing state of the Cooper pairs can make them vulnerable to disruption by inhomogeneities in the material, such as its surface. This will act to ‘break’ apart Cooper pairs, suppressing superconductivity. In the G-L theory, this can be represented with one additional term

$$F = \frac{1}{b} \oint_S |\Delta(r)|^2 \, d^2r + \int_V f[\Delta(r)] \, d^3r, \quad (4.7)$$

which attaches a free energy cost $\propto \frac{1}{b}$ to a nonzero $\Delta$ at the material’s surface. This, in conjunction with the gradient term in equation 4.2, produces a smooth decline in the magnitude of $\Delta$ near the boundary that approximates the suppression with impressive accuracy.

As it happens, we can analytically derive the behaviour of $\Delta$ in this system. If we consider a superconductor that fills the half-space $x > 0$ in Cartesian coordinates, then translational symmetry in the $y$ and $z$ directions will ensure that all physical variation in $\Delta$ will depend solely on $x$. Additionally as $f_n$ is a constant, we may assume without loss of generality that it is zero. Our free energy density is now:

$$f[\Delta(x)] = \alpha|\Delta(x)|^2 + \beta|\Delta(x)|^4 + \frac{\hbar^2}{2m^*} |\partial_x \Delta(x)|^2, \quad (4.8)$$

and our full free energy is

$$F = \frac{1}{b} |\Delta(x = 0)|^2 + \int_0^\infty f[\Delta(x)] \, dx. \quad (4.9)$$

With our assumption that $A = 0$, we have ensured that the phase of $\Delta$ will no longer have any effect on the value of $f$. We may therefore assume that $\Delta$ is real. Using the
Euler-Lagrange equations to find the minima, we obtain:

\[-\alpha \Delta - 2\beta \Delta^3 = \frac{\hbar^2}{2m^*} \partial_x^2 \Delta.\]

Introducing a normalized parameter \(\tilde{\Delta} = \Delta / \Delta_{\text{bulk}}\), this becomes

\[-\tilde{\Delta} + \tilde{\Delta}^3 = \frac{\hbar^2}{2m^*|\alpha|} \partial_x^2 \tilde{\Delta}.\]

To simplify further, we now define a new variable: The characteristic length (sometimes called the coherence length) of the material \(\xi\):

\[\xi = \sqrt{\frac{\hbar^2}{2m^*|\alpha|}}.\] (4.10)

This variable \(\xi\) gives an indication as to the length scale over which \(\Delta\) will return to the bulk value after experiencing some perturbation. Expressing \(x\) in terms of \(\xi\) by introducing \(\tilde{x} = x / \xi\), we obtain

\[-\tilde{\Delta} + \tilde{\Delta}^3 = \partial_x^2 \tilde{\Delta}.\] (4.11)

We now use the identity

\[\partial_x^2 f = \frac{1}{2} \partial_x (\partial_x f)^2,\]

which we use to integrate the previous equation, giving:

\[(\partial_x \tilde{\Delta})^2 = -\tilde{\Delta}^2 + \frac{1}{2} \tilde{\Delta}^4 + C_0,\] (4.12)

where \(C_0\) is a constant. To determine it, we take the bulk case, in which \(\partial_x \tilde{\Delta} = 0\) and \(\tilde{\Delta} = 1\):

\[0 = -1 + \frac{1}{2} + C_0,\]

which gives us

\[C_0 = \frac{1}{2},\]

allowing us to rearrange to

\[(\partial_x \tilde{\Delta})^2 = \frac{1}{2} (\tilde{\Delta}^2 - 1)^2,\] (4.13)

which has a family of solutions of the form \(\tilde{\Delta} = \tanh(\frac{x}{\sqrt{2}} + C_1)\), where \(C_1\) is a constant. Thus, retaining our \(\tilde{x}\) length scale,

\[\Delta(\tilde{x}) = \Delta_{\text{bulk}} \tanh\left(\frac{\tilde{x}}{\sqrt{2}} + C_1\right),\] (4.14)

which is a well-known result [39]. \(C_1\) is a little harder to determine than \(C_0\), but a qualitative understanding is straightforward enough to reach: if there is no suppression at the boundary of the material (e.g. \(b = \infty\)), \(\Delta\) will be at its bulk value for all positive \(x\), and thus \(C_1\) will be infinite. If there is total suppression (e.g. \(b = 0\)), the value of \(\Delta\) at the border will necessarily be zero, and thus \(C_1\) will also be zero. We may thus conclude that \(C_1\) is determined by \(b\). Therefore the effect of boundary suppression in this case is gratifyingly simple: A hyperbolic tangent shape with a magnitude given by \(\Delta_{\text{bulk}}\) and a
rightward shift relative to the $x$-axis dependent on the parameter $b$.

We should now take a moment to consider the characteristic length $\xi$. We have used it to simplify our derivation of the order parameter’s behaviour, but $\xi$ can in fact tell us a great deal about our system. Let us go back to the point where we substituted $\xi$ into our equations:

$$-\Delta + \Delta^3 = \xi^2 \partial_x^2 \Delta,$$

and take the case in which $\Delta$ is almost equal to its bulk value, but deviates fractionally from it:

$$\tilde{\Delta}(x) = 1 - \eta(x)$$

(4.15)

for some $\eta \ll 1$. Expanding our equation and neglecting all nonlinear $\eta$ terms, we obtain

$$-(1 - \eta(x)) + (1 - \eta(x))^3 = -2\eta(x) = -\xi^2 \partial_x^2 \eta(x),$$

(4.16)

which returns the solution for $\eta$ of the form

$$\eta(x) = \eta_0 e^{\pm \frac{\sqrt{2}x}{\xi}}.$$

However, a positive exponent would imply that the perturbation - and thus the order parameter - would increase unboundedly, which is plainly unphysical. Thus the only physically possible solution is

$$\eta(x) = \eta_0 e^{-\frac{\sqrt{2}x}{\xi}},$$

(4.17)

meaning that a small deviation from the bulk value of $\Delta$ will decay away exponentially, with a decay length of $\xi/\sqrt{2}$. This means that the smaller $\xi$ is, the more resistant the superconducting state is to perturbation. This is also well-established [1].

Here we may note that as $\xi$ is proportional to $|\alpha|^{-\frac{1}{2}}$ and $\alpha = \alpha_0(T - T_c)$, as the material approaches the critical temperature $\alpha$ will approach zero and $\xi$ will approach infinity. Thus the closer we are to the superconductor’s critical temperature, the more ‘vulnerable’ the system is to perturbation. At exactly the critical temperature, $\xi$ will be infinite and so the superconductor will never recover from any suppression or perturbation. Again, this is typical behaviour for a 2nd order phase transition in Mean Field Theory [1] [61]. This also tracks exactly with what we may intuitively expect, as at $T_c$ the system is ‘only just’ superconducting and the new state will be vulnerable to disruption. This makes the value of $\xi$ an interesting and important indicator of the stability of any superconducting system.

Despite our new-found knowledge, not every Ginzburg-Landau system is analytically solvable. Many are not, or would simply require an unrealistic amount of work. Therefore in order to examine more complex cases we will have to adjust our approach.

### 4.2 Computationally Minimizing the G-L Free Energy

In the absence of an analytic solution to the behaviour of $\Delta$, we look once more to the core of the Ginzburg-Landau theory: The G-L free energy. If we can minimize it with regard to $\Delta$, that should give us the information we’re looking for.

#### 4.2.1 Discretization

We will be adopting the following computational approach: Using MATLAB, we discretize $\Delta(x)$ over a finite number $N_x$ of equally spaced $x$-values, allowing us to change the integral
for $F$ into a sum and directly minimise it with the fminunc() command to obtain the value of $\Delta$ at each point. By plotting the results against $x$, we may obtain a reasonable understanding of the behaviour of $\Delta(x)$. We therefore make the substitution

$$\Delta(x) \rightarrow \Delta(n),$$  \hspace{1cm} (4.18)

where $\Delta(n)$ is a vector with $N_x$ entries corresponding to the values of $\Delta(x)$ at $N_x$ equally spaced $x$-values. The principal term in our function that may be problematic when discretized is $\partial_x \Delta(x)$. There are many ways of approximating the first derivative of a function while discretizing, but we have opted for

$$\partial_x \Delta(x) \rightarrow \frac{\Delta(n+1) - \Delta(n)}{\delta x},$$  \hspace{1cm} (4.19)

where $\delta x$ is the space between adjacent $x$-values. The choice of $\Delta(n+1) - \Delta(n)$ in the numerator rather than (for instance) $\Delta(n) - \Delta(n-1)$ or $\Delta(n+1) - \Delta(n-1)$, was made to ensure that the gradient for $\Delta(n = 1)$ (i.e. $\Delta$ at the surface) is well-determined and consistent with that of the other points.

Our discretized function has the form

$$F = \frac{1}{b} |\Delta(n = 1)|^2 + \sum_{n=1}^{N_x} \left[ \alpha |\Delta(n)| + \beta |\Delta(n)|^4 \right] + K|M|\Delta|^2, \hspace{1cm} (4.20)$$

where $\Delta$ is a vector of length $N_x$ containing the values of $\Delta(x)$ at each point, $K$ is a constant given by

$$K = \frac{\hbar^2}{2m^*},$$  \hspace{1cm} (4.21)

and $M$ is an $N_x \times N_x$ matrix of the structure:

$$M = \frac{1}{\delta x} \begin{pmatrix} -1 & 1 & 0 & \cdots & 0 & 0 \\ 0 & -1 & 1 & \ddots & 0 & 0 \\ 0 & 0 & -1 & \ddots & 0 & 0 \\ \vdots & \vdots & \ddots & \ddots & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \hspace{1cm} (4.22)$$

Note that the last diagonal element of the matrix is 0, rather than $-1$; as there is no $N_x + 1$ element, having a 1 in the $[N_x, N_x]$ position would result in a cost to the free energy for a nonzero $\Delta(n = N_x)$. This clearly does not correspond to any part of our G-L equations. The lack of an accurate gradient term for the $n = N_x$ position can be effectively mitigated by taking $x$ over a large enough range that $\Delta$ has reached its bulk value by $N_x \delta x$, and thus will have a gradient of 0 anyway.

There is one final change of note made: As we are dealing with spatial increments of $\delta x$, $\Delta(n = 1)$ corresponds to $\Delta$ within $\delta x$ of the boundary. It is therefore impossible to apply a free energy cost to a nonzero $\Delta$ only at the boundary, as any applied cost will also extend to all $\Delta$ within $\delta x$ of it. In order to counteract any error this may introduce and give the same degree of surface suppression for differing $\delta x$-values, our computational $b$ is parameterized as

$$b = b_{\text{const}} \delta x. \hspace{1cm} (4.23)$$
where \( b_{\text{const}} \) is the independent constant that we manually adjust to change the suppression of \( \Delta \) at the boundary.

### 4.2.2 Preliminary Results

A good first step for any simulation is to test its output against the analytic result of a well-known case. Therefore we select for our initial simulation the case of simple boundary suppression solved in the previous chapter. Fig 4.2 is the result, and the closeness of our program’s result and the analytic prediction are an encouraging sign. We may now use our program to test our prediction about the relationship between \( C_1 \) and \( b \), as demonstrated in Fig 4.3. As we predicted, a higher \( b \) shifts the hyperbolic tangent shape of \( \Delta(x) \) to the left. Now that we have confirmed this however we will be measuring surface suppression by percentage of the bulk value at the surface, as this is easier to quantify.

With this replication of analytic predictions, we can be confident that our framework will produce useful results for more esoteric cases. However, there are some caveats.

![Figure 4.2: Good agreement between the theoretical prediction and program results. \( \alpha = -1, \beta = \frac{1}{2}, \xi = 1, \text{ and } b = 10^{-20}, \text{ as close to 0 as the program can tolerate. The inset shows the difference between our computational and analytic } \Delta \text{ values over } x. \Delta \text{ is expressed in units of } \Delta_{\text{bulk}}.](image)

### 4.2.3 Possible Sources of Error

There are two main potential sources of systematic error in our program, and both arise from the gradient term: As alluded to earlier, there are only \( N_x \) \( x \)-values and our gradient is defined in terms of the difference between \( \Delta(n) \) and \( \Delta(n+1) \). We therefore cannot determine the gradient at \( x = N_x \delta x \) and instead simply treat it as 0, effectively assuming
Figure 4.3: Demonstration that increasing $b$ increases $C_2$, and thus $\Delta(x = 0)$, with $\alpha = -1, \beta = \frac{1}{2}, \xi = 1$, and $b$ varied. $\Delta$ is expressed in units of $\Delta_{\text{bulk}}$.

that by $x = N_x \delta x$ we have reached the bulk system. This can lead to inaccuracy if we take $x$ over an insufficient number of characteristic lengths $\xi$ for this assumption to be correct, as displayed in Fig. 4.4a.

Luckily, this form of inaccuracy is comparatively easy to detect and correct by visually examining the plots and increasing the maximum $x$-value, and will not significantly affect the accuracy of our results in plots where $\Delta$ has been allowed to reach its bulk value. The exponential decay experienced by deviations of $\Delta$ from its bulk value aids us here - we do not need to consider large numbers of $\xi$-lengths in order for $\Delta$ to approach its bulk value very closely by $x = N_x \delta x$.

The other, more potentially problematic source of inaccuracy is insufficient detail in our gradient term. Our discretized gradient is only an approximation of the true analytic gradient of the system, and the accuracy of our results rests to a significant degree on how close that approximation is. The more densely our $x$-values are placed, the lower our discrete $\delta x$ value, and the more accurate our gradient approximation. As shown in Fig. 4.2, we can obtain an excellent approximation of the case we are now considering with a $\delta x$ of 0.05. Even a $\delta x$ value of 1 gives a usable (error $\leq 5\%$) result, albeit with significantly less accuracy than those yielded by lower $\delta x$ values (see Fig. 4.4b).

Not every case may be as forgiving as this, however. Therefore as we proceed, we will keep an eye on the $\delta x$ values we use to catch any potential inaccuracies.
4.3 Dominant and Subdominant Parameters

The natural next step for our discretized G-L free energy program is to tackle the case discussed in Section 1.2.1: The time-reversal symmetry breaking appearance of two distinct superconducting states at the surface, which are prevented by symmetry from coexisting in the bulk.

In Ginzburg-Landau terms, this means that there will be more than one order parameter $\Delta$, with each needing to be included in our free energy expression. Each parameter will have its $\alpha$ become negative at a different temperature, and thus would naïvely be expected to appear at different critical temperatures.

However in addition to different critical temperatures, one order parameter - the one with the higher critical temperature - will have a lower bulk free energy and due to the competition between the order parameters will block the appearance of the other in the system’s bulk state. This would seem to preclude the realization of our hypothetical additional order parameter, but if the energetically-preferable order parameter is locally suppressed - such as near a boundary, as it is in the case considered above - it may be energetically advantageous for the other order parameter to appear in that area.

We will be denoting the order parameter with the lower bulk free energy - or the ‘dominant’ order parameter - $\Delta_d$, and order parameter with the higher bulk free energy - the ‘sub-dominant’ order parameter - $\Delta_s$, as we are currently agnostic as to their spin properties. In this section we are considering a model of two competing order parameters in which only $\Delta_d$ is expressed in the bulk. That is, the free energy of the bulk of the system must be lower for a pure $\Delta_d$-state than for a pure $\Delta_s$-state or any mixture of the two. The total free energy of the system will now be the free energy of each individual order parameter plus the free energy of their interaction. In equation form, we write:

$$F[\Delta_d, \Delta_s] = F_d + F_s + F_{ds},$$

(4.24)
where the first two terms in eq. 4.24 are the individual free energies. These are of the form given by eqs. 4.8 and 4.9, but $\Delta_d$ is suppressed at the surface while $\Delta_s$ is not:

$$
F_d = \frac{1}{b} |\Delta_d(0)|^2 + \int_0^\infty \alpha_d |\Delta_d|^2 + \beta_d |\Delta_d|^4 + \frac{\hbar^2}{2m_d^*} |\partial_x \Delta_d|^2 \, dx ,
$$

(4.25)

$$
F_s = \int_0^\infty \alpha_s |\Delta_s|^2 + \beta_s |\Delta_s|^4 + \frac{\hbar^2}{2m_s^*} |\partial_x \Delta_s|^2 \, dx .
$$

(4.26)

The ambiguous interpretation of the ‘effective mass’ $m^*$ means that in general we should allow for the possibility of different values for $m_d^*$ and $m_s^*$. The $F_{ds}$ term describes the interaction between the states, and takes the form

$$
F_{ds} = \int_0^\infty \gamma_1 |\Delta_d|^2 |\Delta_s|^2 + \gamma_2 (\Delta_d^2 \Delta_s^* + \Delta_d^* \Delta_s^2) \, dx ,
$$

(4.27)

where $\gamma_1$ and $\gamma_2$ are positive constants and $\Delta^*$ denotes the complex conjugate of $\Delta$. We are only including fourth-order interactions between $\Delta_d$ and $\Delta_s$ here, as we assume both behave differently under lattice symmetries, which will forbid lower-order interactions [17]. The $\gamma_1$ term is quite straightforward, imposing a quadratic free energy cost to both $\Delta_d$ and $\Delta_s$ concurrently being nonzero. The $\gamma_2$ term is more interesting, however: it represents the first time so far that the phases of our order parameters have become important. The phase behaviour of this system may be elucidated by a change of perspective: if we recall the first time so far that the phases of our order parameters have become important. The ambiguous interpretation of the ‘effective mass’ $m^*$ means that in general we should allow for the possibility of different values for $m_d^*$ and $m_s^*$. The $F_{ds}$ term describes the interaction between the states, and takes the form

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F_{ds} = \int_0^\infty \gamma_1 |\Delta_d|^2 |\Delta_s|^2 + \gamma_2 (\Delta_d^2 \Delta_s^* + \Delta_d^* \Delta_s^2) \, dx ,
$$

(4.27)

where $\gamma_1$ and $\gamma_2$ are positive constants and $\Delta^*$ denotes the complex conjugate of $\Delta$. We are only including fourth-order interactions between $\Delta_d$ and $\Delta_s$ here, as we assume both behave differently under lattice symmetries, which will forbid lower-order interactions [17]. The $\gamma_1$ term is quite straightforward, imposing a quadratic free energy cost to both $\Delta_d$ and $\Delta_s$ concurrently being nonzero. The $\gamma_2$ term is more interesting, however: it represents the first time so far that the phases of our order parameters have become important. The phase behaviour of this system may be elucidated by a change of perspective: if we recall that we can write a complex order parameter $\Delta$ as $|\Delta|e^{i\phi}$, we may rewrite the $\gamma_2$ term as follows:

$$
\gamma_2 (\Delta_d^2 \Delta_s^* + \Delta_d^* \Delta_s^2) = \gamma_2 |\Delta_d|^2 |\Delta_s|^2 (e^{i2(\phi_d - \phi_s)} + e^{-i2(\phi_d - \phi_s)})
$$

(4.28)

$$
= \gamma_2 |\Delta_d|^2 |\Delta_s|^2 2 \cos(2[\phi_d - \phi_s]),
$$

which implies that if the difference between the phases of $\Delta_d$ and $\Delta_s$ is $\frac{\pi}{2}$, $\cos(2[\phi_d - \phi_s])$ will be equal to $-1$ and therefore reduce the free energy. This makes $\phi_d - \phi_s = \pm \frac{\pi}{2}$ the preferred phase difference of the system. Without loss of generality, we may set $\phi_d = 0$, which will result in a $\phi_s$ of $\pm \frac{\pi}{2}$; this gives a wholly real $\Delta_d$ and a wholly imaginary $\Delta_s$. As taking the complex conjugate of an imaginary $\Delta_s$ will give $-\Delta_s$, the condition eq. 1.2 is broken and the expression of $\Delta_s$ in our system will result in the TRSB proposed by the aforementioned researchers [27,34,37].

If we group our second-order $\Delta_s$-terms for this case together, we now obtain

$$
(\alpha_s + [\gamma_1 - 2\gamma_2] |\Delta_d|^2) |\Delta_s|^2 ,
$$

(4.29)

allowing us to define an ‘effective $\alpha_s$’ of $(\alpha_s + [\gamma_1 - 2\gamma_2] |\Delta_d|^2)$. $\Delta_s$ can only appear if this ‘effective $\alpha_s$’ is negative (while this does not take into account the effects of the gradient terms, it still gives a good qualitative understanding of the system). This condition becomes easier to satisfy if $|\Delta_d|^2$ is suppressed, as it is near our boundary. Thus, we expect $\Delta_s$ to appear only near the surface of our superconductor.

We now know how the phases of our order parameters will behave under these circumstances. But how will the order parameters themselves behave near the surface? To find out, we discretize

$$
\Delta_d(x) \rightarrow \Delta_d(n)
$$

$$
\Delta_s(x) \rightarrow \Delta_s(n),
$$

(4.30)

and use fminunc() to minimize the free energy as before. The gradient terms will be
§4.3 Dominant and Subdominant Parameters

the same as the previous chapter, and because the phase difference between our order parameters will be constant we are able to deal solely with their magnitudes as we minimize the free energy. Manfred Sigrist, in a paper that deals with a system similar to ours, calculates that provided $\Delta_s \ll \Delta_d$, the form of $\Delta_s$ will be [39]:

$$\Delta_s(x) \propto \cosh^{-\zeta} \left( \frac{x}{\sqrt{2}\xi_d} \right), \quad (4.31)$$

where

$$\zeta = \frac{\xi_d}{\xi_s} \quad (4.32)$$

is the ratio of the characteristic lengths of $\Delta_d$ and $\Delta_s$. The amplitude of the hyperbolic cosine term is temperature-dependent and extremely difficult to quantify analytically. Note that this assumes that $\Delta_d$ will not be significantly affected by $\Delta_s$. This is reasonable, as Sigrist is dealing with the case $\Delta_s \ll \Delta_d$. Our results as displayed in Fig 4.5 are excellently in accordance with Sigrist’s prediction. Our qualitative predictions are borne out as well: $\Delta_s$ is only non-zero around the region where $\Delta_d$ is suppressed, and dies away to zero in the bulk. We may now be rather proud of our program; it has successfully replicated the analytic predictions of two quite dissimilar cases. But can we be sure of its reliability?

4.3.1 Accuracy

With the introduction of a second order parameter, now is a good time to revisit the question of accuracy in our new, more complex system.

As we can see in Fig. 4.5, both $\Delta_s$ and $\Delta_d$ have reached their bulk values by the position $x = N_x \delta x$. This means we can be reasonably assured that our assumption that the gradient is very close to zero at $x = N_x \delta x$ is not going to be the cause of any inaccuracy in our results. The gradient term itself, however, requires more examination. The single-$\Delta$ system explored Section 4.2.2 required only a $\delta x$ of 0.05 to replicate the analytic prediction extremely accurately. However, the two-order-parameter system explored in this chapter requires a $\delta x \sim 0.0167$ for comparable accuracy. Indeed, for higher $\delta x$ the program can give quite different magnitudes for $\Delta_s(n = 1)$ (see Fig. 4.6a).

Why? This actually has to do with the value we have chosen for $\gamma_1$: As we can see in Fig. 4.6b, there is a critical value for $\gamma_1$ beyond which $\Delta_s$ is totally suppressed everywhere. The value used in Fig. 4.5 is very close to this critical value in order to satisfy Sigrist’s condition of $|\Delta_s| \ll |\Delta_d|$, but as a result a small deviation to the left or right of this point in Fig. 4.6b will result in a very large deviation in $|\Delta_s|$. Higher values of $\delta x$ can shift us along Fig. 4.6b, as information about the gradient of the system is lost. We may reasonably suppose, therefore, that lower values of $\gamma_1$ would result in a smaller variance for high $\delta x$ - and indeed they do.

4.3.2 The Magnetic Order Parameter

We have until this point assumed that the magnetic vector potential $A = 0$, which seems reasonable enough. However magnetism is often associated with TRSB, as a magnetic field explicitly breaks Time-Reversal symmetry. Indeed, Timm at al. and others have predicted the emergence of a spontaneous current at the edges of a superconductor with the properties we are interested in [53] [63].
In contrast to the supercurrent carried a superconductor, this current does not require the application of any external field. However, the magnetic field produced by this current must be screened in the bulk of the superconductor in accordance with the Meissner effect, and this requires the development of screening currents at the edges which propagate in the opposite direction to the spontaneous currents. Including these screening currents requires us to consider a non-zero magnetic vector potential $\mathbf{A}$ in the Ginzburg-Landau equations.

The first thing we must include in our updated free energy is the $\mathbf{B}$-term from eq. 4.2, which applies an energy cost to a non-zero magnetic field $[1]:$

$$
\frac{(\nabla \times \mathbf{A})^2}{8\pi}.
$$

(4.33)

However, we must remember that our superconductor fills the half-space $x > 0$, so there can be no variation in $\mathbf{A}$ in the $y$ or $z$ directions. In other words the derivative of any part of $\mathbf{A}$ in those directions must be zero. Taking this into account we can calculate

$$
\nabla \times \mathbf{A} = (0, -\partial_z A_z, \partial_z A_y),
$$

(4.34)
§4.3 Dominant and Subdominant Parameters

Decreasing $dx$

(a)

Figure 4.6: Demonstration of the accuracy requirements of our new system. a) is a plot of $\Delta_d$ and $\Delta_s$ vs $x$ with $\alpha_d = -2, \beta_d = 1, \xi_d = \frac{1}{\sqrt{2}}, \alpha_s = -0.7, \beta_s = 0.3, \xi_s = \frac{1}{\sqrt{0.7}},$ and $\gamma_1 = 1.04$. Taken over 100, 200, 300, and 400 $x$-values, each of which resulted in a different one of the dashed lines.

b) is a plot of $\Delta_s$ at the boundary vs $\gamma_1$ for 600 $x$-values ($\delta x \approx 0.0167$) and 100 $x$-values ($\delta x = 0.1$). Smaller values of $\delta x$ do not produce a significantly different result to $\delta x \approx 0.0167$. The same values of $\alpha_d, \alpha_s, \beta_d, \beta_s$ etc. were used as (a). The $\gamma_1$ value we have been using so far is marked with an arrow. $\Delta_d$ and $\Delta_s$ are expressed in units of $\Delta_{d,\text{bulk}}$.

and by rotating our coordinate system around the $x$-axis, we can set $A_z = 0$, ensuring that $A = (A_x, A_y, 0)$ and that $(\nabla \times A)^2 = (\partial_x A_y)^2$.

The second thing we must change in order to incorporate $A$ is our ‘gradient term’ [1]. In the full one-state G-L free energy, including $A$ changes

$$\frac{\hbar^2}{2m^*} |\nabla \Delta|^2$$

to

$$\frac{\hbar^2}{2m^*} \left| (i\nabla - \frac{e^*}{c\hbar} A) \Delta \right|^2,$$

(4.35)

but we must be careful: We have only been dealing with $\Delta$ variation in the $x$-direction, so it is easy to forget that strictly, the term $(i\nabla + \frac{e^*}{c\hbar} A) \Delta$ is a vector. Thus when we take the absolute square of it, this will group the $A_x$ terms with the $\partial_x$ terms, and the $A_y$ terms with the $\partial_y$ terms. However we know that $A_x$ doesn’t feature in the $\nabla \times A$ term, so to minimize this term $A_x$ can (and must) be zero. Therefore $A = (0, A_y, 0)$. Furthermore - by our $x > 0$ half-space stipulation - the only part of $\nabla \Delta$ that is non-zero is $\partial_x \Delta$. Thus we can write the above term as

$$\frac{\hbar^2}{2m^*} \left( |i\partial_x \Delta|^2 + \left| \frac{e^*}{c\hbar} A_y \Delta \right|^2 \right).$$

(4.36)

There is one final term we haven’t yet accounted for: The second-order gradient term [39].
Allowing variation of the gap in both $x$ and $y$ directions, Sigrist found this term is
\[
K_{ds} \left[ \left( i \partial_x - \frac{e^s}{c \hbar} A_x \right) \Delta_s \left( -i \partial_y - \frac{e^s}{c \hbar} A_y \right) \Delta_d^* + \left( i \partial_y - \frac{e^s}{c \hbar} A_y \right) \Delta_s \left( -i \partial_x - \frac{e^s}{c \hbar} A_x \right) \Delta_d^* + c.c. \right], \quad (4.37)
\]
for some real constant $K_{ds}$ [6]. In our $x > 0$ half-space system where $\partial_y \Delta_{d/s} = 0$ this takes the form
\[
K_{ds} \frac{e^s}{c \hbar} A_y \left[ i (\partial_x \Delta_d^*) \Delta_s + i (\partial_x \Delta_s^*) \Delta_d - i (\partial_x \Delta_d) \Delta_s^* - i (\partial_x \Delta_s) \Delta_d^* \right]. \quad (4.38)
\]
When our order parameters have non-zero gradients and a non-zero phase difference this creates a first-order coupling between them and $A_y$, generating a non-zero $A_y$ close to the surface.

Our new free energy is therefore
\[
F[\Delta_d, \Delta_s] = F_d + F_s + F_{ds} + F_M, \quad (4.39)
\]
for
\[
F_M = \int_{0}^{\infty} K_{ds} \frac{e^s}{c \hbar} A_y \left[ i (\partial_x \Delta_d^*) \Delta_s + i (\partial_x \Delta_s^*) \Delta_d - i (\partial_x \Delta_d) \Delta_s^* - i (\partial_x \Delta_s) \Delta_d^* \right] + \frac{(\partial_x A_y)^2}{8\pi} + \frac{e^2}{2m^*_c} |A_y\Delta_s|^2 + \frac{e^2}{2m^*_c} |A_y\Delta_d|^2. \quad (4.40)
\]
Incorporating these new terms into the free energy and minimizing it gives Fig. 4.7, which indeed displays the appearance of a non-zero magnetic vector potential near the surface, decaying away to zero in the bulk. It does this over a slightly longer distance than $\Delta_s$ does, but we can credit this to the $\nabla \times A^2$ term preventing a faster decay. Comparing Figs. 4.5 and 4.7, we can see that a non-zero $A_y$ slightly increases the magnitude of the peak of $\Delta_s$ but does not seem to impact its decay length. The magnetic field and current generated by this magnetic field are given by Fig. 4.8, and we can see that these results agree with the Meissner effect - we have not applied an external magnetic field, and integrating $J_y$ shows that the total current is zero, as is required.

Having successfully incorporated the magnetic vector potential, we are now in a good position to move forward and begin assessing the non-centrosymmetric system described by Timm. et al. [53]. This would in principle be quite straightforward - we would simply need to add a negative second-order interaction term $\alpha_{ds}$ to $F_{ds}$:
\[
F_{ds} = \int_{0}^{\infty} \gamma_1 |\Delta_d|^2 |\Delta_s|^2 + \gamma_2 (|\Delta_d^2\Delta_s^2 + \Delta_d^2 \Delta_s^2|) + \alpha_{ds} (\Delta_d \Delta_s^* + \Delta_d^* \Delta_s) dx,
\]
which would enable $\phi_d - \phi_s$ values other than $\pi$ to appear, as the $\gamma_2$ and $\alpha_{ds}$ terms are minimized by different phases. However doing so now would yield only limited insight, as to accurately describe a real system would require currently-unknown constraints on the G-L coefficients.

Despite our successes so far, astute readers may have noticed a problem: The Ginzburg-Landau theory, for all its many strengths, is wholly phenomenological and thus dependent on measurements to ensure a resemblance to physical systems. The system proposed by
Figure 4.7: $\Delta_d$, $\Delta_s$, and $A_y$ for $\alpha_d = -2, \beta_d = 1, \xi_d = \frac{1}{\sqrt{2}}, \alpha_s = -0.7, \beta_s = 0.3, \xi_s = \frac{1}{\sqrt{1.04}}, \gamma_1 = 1.04, K_{ds} = 0.16,$ and $\gamma_2 = 0$. The magnetic vector potential is expressed in units of $10 \frac{A}{c^2}$. $\Delta_d$ and $\Delta_s$ are expressed in units of $\Delta_d, \text{bulk}$.

Timm et al. is at present wholly theoretical, and as such we have no measurements to guide us. How are we to ensure our simulation bears any resemblance to real systems? Our luck holds. There is a technique that will allow us to connect the microscopic Bogoliubov Hamiltonian of the previous chapter to the G-L free energy we have dealt with here: The Linked Cluster Expansion.
Figure 4.8: $A_y$, $B_z$, and $J_y$ for $\alpha_d = -2, \beta_d = 1, \xi_d = \frac{1}{\sqrt{2}}, \alpha_s = -0.7, \beta_s = 0.3, \xi_s = \frac{1}{\sqrt{0.7}}, \gamma_1 = 1.04, K_{ds} = 0.4, \text{ and } \gamma_2 = 0$. $A_y$ is expressed in units of $10 \frac{\Delta}{c_x}$, $B_z$ is expressed in terms of $10 \frac{\Delta}{c_x} m^{-1}$, and $J_y$ is expressed in units of $10 \frac{\Delta}{c_x} m^{-2}$.
Chapter 5

The Bulk Linked Cluster Expansion

In the previous chapter, we were introduced to the Ginzburg-Landau theory and learned of its flexibility and power in describing complex superconducting systems. However, we also noted that due to its phenomenological nature it alone could not be used to accomplish our aims. In this chapter we will learn of the solution to our dilemma: The Linked Cluster Expansion.

5.1 Singlet s-wave Case

The Linked Cluster Expansion theorem states that we can write the thermodynamic potential of our system as an expansion in the potential term $\hat{V}$:

$$\Omega = \Omega_0 - \frac{1}{\beta} \sum_{l=1}^{\infty} U_l,$$  

(5.1)

in which $\Omega$ is the full thermodynamic potential, $\Omega_0$ is the unperturbed (and thus non-superconducting) potential, and

$$U_l = \frac{(-1)^l}{l!} \int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_l \langle T_{\tau} \hat{V}(\tau_1) \cdots \hat{V}(\tau_l) \rangle_{\text{con.}},$$  

(5.2)

where the $\text{con.}$ subscript denotes that we only count terms that result in connected Feynman diagrams [54]. Feynman diagrams are a way of representing Green’s functions and other microscopic interactions diagrammatically. They are very powerful and flexible, but we will only be using a small fraction of their capability here. Each Green’s function of two $\tau$ values $G(k; \tau_1 - \tau_2)$ is drawn connecting them (as in Fig. 5.1), and can be taken as representing an electron moving through the system. Other interactions can be represented by dotted or dashed lines, such as $\Delta$ - which we’ve already established is a pairing potential for the breaking of a Cooper pair and the release of two electrons into the system. Thus $|\Delta|^2 G(k; \tau_1 - \tau_2)G(-k, \tau_1 - \tau_2)$ is represented by the diagram shown in

![Figure 5.1: A Green’s function as it is represented in Feynman diagrams](image-url)
This diagram is 'connected', as all of its elements are linked together in some way. In contrast, the fourth-order diagram Fig. 5.3 is 'disconnected', as it consists of two separate parts not joined by any lines. These diagrams will not contribute to the Linked Cluster Expansion, as they will all cancel out. The proof for this is rather complex and not particularly helpful in understanding this thesis, so it will not be presented here. For those interested, it can be found in Mahan along with a derivation of the Linked Cluster Expansion itself [54].

We will be taking only the second and fourth orders of our Linked Cluster Expansion \((l = 2, 4)\), as the smallness of \(\Delta\) renders higher orders negligible, and odd values of \(l\) will result in a trace over an unequal number of creation and annihilation operators which just gives zero. While our definition of \(\Delta\) depends on the trace over two lone creation operators being nonzero, this is not inconsistent - \(U_l\) uses \(\langle 0 |\), which is a trace over the unperturbed states, while \(\Delta\) uses \(\langle \rangle\), which is a trace over the true states, and can thus give non-zero expectation values for expressions with unequal numbers of creation and annihilation operators.

We will be starting with the s-wave singlet case considered in Section 3.1.
5.1.1 Analytic Work

Recall that in Chapter 3 we found the Bogoliubov Hamiltonian for the s-wave singlet superconductor is

\[ H = H_0 + \frac{N}{V} |\Delta|^2 + \tilde{V}, \]

with

\[ \tilde{V} = \sum_k \Delta C_{k\uparrow}^\dagger C_{-k\downarrow}^\dagger + \Delta^\dagger C_{-k\downarrow} C_{k\uparrow}. \]

In Chapter 3 we evaluated the full thermodynamic potential; we will now approximate it using the Linked-Cluster Expansion. We take \( U_2 \) first:

\[ U_2 = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \langle T_\tau \tilde{V}(\tau_1)\tilde{V}(\tau_2) \rangle_{\text{con.}}. \]

We now expand \( \tilde{V} \) to obtain

\[ U_2 = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_{k,k'} 0 \langle T_\tau [\Delta C_{k\uparrow}^\dagger(\tau_1)C_{-k\downarrow}^\dagger(\tau_1) + \Delta^\dagger C_{-k\downarrow}(\tau_1)C_{k\uparrow}(\tau_1)] \]
\[ \times [\Delta C_{k'\uparrow}(\tau_2)C_{-k'\downarrow}(\tau_2) + \Delta^\dagger C_{-k'\downarrow}(\tau_2)C_{k'\uparrow}(\tau_2)] \rangle_{\text{con.}}, \]

and then take only the expanded terms which have equal numbers of creation and annihilation operators:

\[ U_2 = \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_k 0 \langle T_\tau [\Delta^2 C_{-k\downarrow}^\dagger(\tau_1)C_{-k\downarrow}^\dagger(\tau_2)C_{k\uparrow}(\tau_1)C_{k\uparrow}(\tau_2) \]
\[ + C_{-k\downarrow}(\tau_1)C_{k\uparrow}(\tau_1)C_{k'\uparrow}(\tau_2)C_{-k'\downarrow}(\tau_2)] \rangle_{\text{con.}}. \]

As \( 0 \langle C_{k\sigma} C_{k'\sigma'} \rangle \) gives zero for \( \sigma \neq \sigma' \), we require \( k = k' \) to obtain non-zero results. With standard rearranging and \( \tau \) variable relabelling, this can be written

\[ U_2 = \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_k 0 \langle T_\tau [\Delta^2 C_{-k\downarrow}^\dagger(\tau_1)C_{-k\downarrow}^\dagger(\tau_2)C_{k\uparrow}(\tau_1)C_{k\uparrow}(\tau_2)] \rangle_{\text{con.}}, \]

and evaluating the trace using Wick’s theorem gives

\[ U_2 = \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_k |\Delta^2 G^{(0)}(k, \tau_1 - \tau_2)G^{(0)}(-k, \tau_1 - \tau_2)|. \]

This corresponds to the Feynman diagram shown in Fig. 5.2. We now use the non-interacting Green’s function Fourier transform properties eq. 2.18 and eq. 2.23 to obtain

\[ U_2 = \frac{1}{\beta^2} |\Delta|^2 \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_k \sum_{n,n'} e^{-i(\omega_n + \omega_n')(\tau_1 - \tau_2)} \frac{1}{i\omega_n - \xi_k} \frac{1}{i\omega_n' - \xi_{k'}}. \]

Evaluating the integrals gives a factor of \( \beta^2 \delta_{n,n'} \), so

\[ U_2 = |\Delta|^2 \sum_k \sum_n \frac{1}{\omega_n^2 + \xi_k^2}. \]
To evaluate the sum over $n$, we recall that for fermions

$$\omega_n = \frac{(2n + 1)\pi}{\beta},$$

obtaining

$$U_2 = \beta |\Delta|^2 \sum_k \frac{\tanh \left( \frac{\beta \nu_k}{2} \right)}{2\xi_k}.$$  \hspace{1cm} (5.10)

We now turn our attention to $U_4$:

$$U_4 = \frac{1}{4!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \sum_{k, k', k''} C_{k^\prime}(\tau_1)C_{k^\prime}(\tau_2)C_{k^\prime}(\tau_3)C_{k^\prime}(\tau_4)$$

which expands to

$$U_4 = \frac{1}{24} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \sum_{k, k', k''} 0 \langle T_\tau \rangle \Delta^4$$

which, once again taking only the terms with equal numbers of creation annihilation operators and using both rearrangement and $\tau$ variable relabelling gives

$$U_4 = \frac{1}{4!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \sum_k |\Delta|^4$$

as $k = k' = k'' = k'''$ for non-zero, connected results.

This is where only counting connected diagrams comes in: Wick’s theorem decomposes the trace into four terms, comprising two identical copies of two different diagrams. However, one of these diagrams is a disconnected diagram comprising two copies of the one in Fig 5.2 (see Fig.5.3), and is thus discarded. The other can be seen in Fig. 5.4, and gives us the expression

$$U_4 = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \sum_k |\Delta|^4$$

We repeat our trick with the Fourier transform properties and integrals, obtaining

$$U_4 = \frac{1}{2} |\Delta|^4 \sum_k \sum_n \frac{1}{(\omega_n^2 + \xi_k^2)^2} = \beta |\Delta|^4 \sum_k \frac{\text{sech}^2(\frac{\xi_k \beta}{2}) (\xi_k \beta - \sinh(\xi_k \beta))}{16 \xi_k^4}.$$  \hspace{1cm} (5.15)

Now that we can construct an expression for the free energy per particle of the form
we can begin to connect this to the G-L free energy (the subscript $s$ is once again being used to denote ‘singlet’).

5.1.2 Computational Work

It is apparent that in the equation above that $\alpha_s = \frac{1}{V} - \frac{1}{N} V^2 \Delta$ and $\beta_s = -\frac{1}{N} V^4 \Delta^4$, but how are we to determine our $U$ values? Again, we turn to the two-dimensional tight-binding approximation. In this model,

$$\alpha_s = \frac{1}{V} - \frac{1}{N} \sum_{k_x,k_y} \tanh\left(\frac{\beta \xi_k}{2}\right) \frac{2\xi_k}{2\xi_k} \tag{5.17}$$

and

$$\beta_s = -\frac{1}{N} \sum_{k_x,k_y} \xi_k \beta \text{sech}^2\left(\frac{\xi_k \beta}{2}\right) - 2 \tanh\left(\frac{\xi_k \beta}{2}\right) \frac{16 \xi_k^3}{16 \xi_k^3} \tag{5.18}$$

Note that we have made a notation change in $\beta_s$ that allows MATLAB to deal with the sum. The variables $\alpha_s$ and $\beta_s$ are now functions only of the temperature $T$, and we have enough information to plot them; Fig. 5.5 and Fig. 5.6 show $\alpha_s$ and $\beta_s$ vs $k_B T$, respectively.

From these we can see that the critical temperature - i.e., the temperature at which $\alpha_s$ becomes negative and creates the conditions for a non-zero $\Delta$ - is approximately $10^{-3}$, just as we predicted in Chapter 2. In fact, examining the Grand Canonical Ensemble $T_c$ condition given in eq. 3.20, we find that it is identical to the expression we have just derived for $\alpha_s$:

$$\frac{1}{V} - \frac{1}{N} \sum_k \frac{1}{2\xi_k} \frac{1}{\xi_k (1 + e^{\beta \xi_k})} = \frac{1}{V} - \frac{1}{N} \sum_k \tanh\left(\frac{\beta \xi_k}{2}\right) \frac{2\xi_k}{2\xi_k} \tag{5.19}$$

This is exactly what we expect from the expansion, and should give us confidence that we are on the right track.

We can also observe that according to our model, $\beta_s$ diverges as we approach $T = 0$. 

\[\frac{1}{N} \Omega = \frac{1}{N} \Omega_0 + \alpha_s |\Delta|^2 + \beta_s |\Delta|^4, \tag{5.16}\]
Figure 5.5: $\alpha_s$ vs $k_B T$ for $N = 2000, V = 0.4$, and $\mu = 0.3$. $k_B T$ is in units of $2t$. The inset is a focus around the critical temperature $T_c \approx 1e^{-3}$. A line at 0 on the $y$-axis has been added to enable the discernment of $T_c$. $\alpha_s$ is in units of $1/2t$.

This is not a problem, as we only expect our G-L inspired model to be accurate around the critical temperature $T_c$ - the higher-order $\Delta$ terms will grow more significant at low $T$. We may be able to extend the validity of our model by including higher orders in $\Delta$, but in accordance with the G-L theory we are only taking up to $|\Delta|^4$. We can now compare the predictions for $\Delta$ given by the G-L coefficients obtained from the LCE and the mean-field technique used previously. In Fig. 5.7, the predicted $\Delta$ values for both the G-L and mean-field methods are plotted against $k_B T$, and we can see that they agree very well close to $T_c$ but diverge below about $0.55T_c$, this divergence becoming significant at $0.55T_c$. The G-L method’s $\Delta$ predictions’ divergence from the mean-field predictions by dying away to zero at $T = 0$ is a direct consequence of $\beta_s$ ‘blowing up’ so dramatically.

So our LCE-derived G-L treatment of the singlet pairing case is quite accurate, at least as long as we stick reasonably close to the critical temperature! This is rather heartening, and indicates that we are now ready to deal with a more complex case.
§5.1 Singlet s-wave Case

Figure 5.6: $\beta_s$ vs $k_B T$ for $N = 2000^2, V = 0.4$, and $\mu = 0.3$. $k_B T$ is in units of $2t$. The inset is a focus around $T_c \approx 1e^{-3}$. $\beta_s$ is in units of $1/(2t)^3$.

Figure 5.7: Predicted $\Delta$ for both BCS and GCE methods vs $k_B T$ for $N = 2000^2, V = 0.4$ and $\mu = 0.3$. $k_B T$ and $\Delta$ are in units of $2t$. The inset shows a focus around $T_c \approx 1e^{-3}$. 

5.2 Non-centrosymmetric Superconductors

Now that we have illustrated our technique and shown that our LCE approximation agrees with the full mean-field theory treatment, it is time to apply it to a non-centrosymmetric system - the case designed too complex to deal with using the grand canonical ensemble in Section 3.2.

5.2.1 Analytic Work

As noted in Chapter 3, the $\hat{V}$ for this system is

$$\hat{V} = \frac{1}{2} \sum_{k} \left[ \Delta_{s}^{+} \left( C_{k^\uparrow} C_{-k^\downarrow} - C_{k^\downarrow} C_{-k^\uparrow} \right) + \Delta_{s}^{-} \left( C_{-k^\uparrow} C_{k^\downarrow} - C_{-k^\downarrow} C_{k^\uparrow} \right) \right]$$

$$+ \Delta_{t} \left( l_{k} C_{k^\uparrow} C_{-k^\uparrow} - l_{k}^{*} C_{k^\downarrow} C_{-k^\downarrow} \right) + \Delta_{t}^{*} \left( l_{k}^{*} C_{-k^\uparrow} C_{k^\downarrow} - l_{k} C_{-k^\downarrow} C_{k^\uparrow} \right)$$

for symmetry factor

$$l_{k} = \sin(k_y a) - i \sin(k_x a).$$

Simply applying the Linked Cluster Expansion to this would be very messy, and result in us having to deal with many ‘cross terms’ involving both $\Delta_{t}$ and $\Delta_{s}$. However, we may ameliorate this with the transformation used in Chapter 3. Applying it, we obtain:

$$\hat{V} = \hat{V}^{-} + \hat{V}^{+},$$

where

$$\hat{V}^{\pm} = \frac{1}{2} \sum_{k} \left[ C_{k}^{\pm \dagger} C_{-k}^{\pm} \Delta_{k}^{\pm} + C_{-k}^{\pm} C_{k}^{\pm \dagger} \Delta_{k}^{\pm} \right]$$

and

$$\Delta_{k}^{\pm} = \Delta_{s}^{\pm} |l_{k}| \Delta_{t}^{\pm}.$$ (5.24)

This will give Greens functions of the form

$$G^{\pm}(k, i\omega_{n}) = \frac{1}{i\omega_{n} - \xi_{k}^{\pm}}$$

for

$$\xi_{k}^{\pm} = \xi_{k}^{\pm} \pm \lambda |l_{k}|$$

(5.26)

(due to the structure of $\vec{g}_{k}$, this definition is equivalent to that given in eq. 3.26). As in Chapter 3 the constant $\lambda$ is determined by the symmetries present in the system; in a centrosymmetric system, $\lambda = 0$ and $\xi_{k}^{+} = \xi_{k}^{-}$. We expect this to reproduce the behaviour we found in our G-L simulations in the previous chapter, with both order parameters appearing at the surface but only one expressed in the bulk. However, inversion symmetry breaking will result in non-degenerate energies $\xi_{k}^{+} \neq \xi_{k}^{-}$ via a non-zero $\lambda$ and the coexistence of $\Delta_{t}$ and $\Delta_{s}$ everywhere.

The $\Delta_{k}^{\pm}$ formulation has several advantages. First, it explicitly shows that the singlet and triplet order parameters are mixed, and not simply separate and non-interacting. Second, the $\pm$ creation and annihilation operators anticommute, and thus are independent; we can therefore treat the $+$ and $-$ parts of the upcoming $U_{l}$ expressions completely separately. The $\hat{V}^{+} + \hat{V}^{-}$ structure of our new $\hat{V}$ is rather remarkable - it implies that not only...
is the pairing potential diagonal in the $\Delta_4$ basis, but so is the normal state Hamiltonian. It should be noted however that not all parts of the free energy have been changed by our transformation - there still remain the terms $\frac{N}{V}|\Delta_s|^2$ and $\frac{N}{N}|\Delta_t|^2$, analogous to the $\frac{N}{V}|\Delta|^2$ term in the previous section. This is not a problem, as after the Linked Cluster Expansion is complete we will be transforming back into the $t/s$ basis.

Our new $U_2$ is given by

$$U_2 = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \left[T_\tau \hat{V}^+(\tau_1) \hat{V}^+(\tau_2) + \hat{V}^-(\tau_1) \hat{V}^-(\tau_2) + \hat{V}^+(\tau_1) \hat{V}^-(\tau_2) + \hat{V}^-(\tau_1) \hat{V}^+(\tau_2)\right]_{\text{con.}}, \tag{5.27}$$

but the $\hat{V}^+ \hat{V}^-$ parts are zero because of the aforementioned $\pm$ independence, so

$$U_2 = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \left[T_\tau \hat{V}^+(\tau_1) \hat{V}^+(\tau_2) + \hat{V}^-(\tau_1) \hat{V}^-(\tau_2)\right]_{\text{con.}}. \tag{5.28}$$

This should be familiar - we essentially have $+$ and $-$ versions of the $U_2$ term from the singlet-only case, with nearly identical Feynman diagrams (see Fig. 5.8). This naturally gives separate $U_2^\pm$ terms:

$$U_2 = U_2^+ + U_2^- \tag{5.29},$$

where

$$U_2^\pm = \beta \sum_k |\Delta_k^\pm|^2 \frac{\tanh\left(\frac{\beta \xi_k}{2}\right)}{4 \xi_k^\pm}. \tag{5.30}$$

Note that this looks like half of our previous $U_2$. This means that if we take $|l_k| = 0$, $U_2^+ = U_2^-$ and we recover eq. 5.10.

![Figure 5.8: Feynman diagram for $U_2^\pm$](image)

We now take the $l = 4$ case:

$$U_4 = \frac{1}{4!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \left[T_\tau \hat{V}^+(\tau_1) \hat{V}^+(\tau_2) \hat{V}^+(\tau_3) \hat{V}^+(\tau_4) + \hat{V}^-(\tau_1) \hat{V}^-(\tau_2) \hat{V}^-(\tau_3) \hat{V}^-(\tau_4) + 6 \hat{V}^+(\tau_1) \hat{V}^+(\tau_2) \hat{V}^-(\tau_3) \hat{V}^-(\tau_4)\right]_{\text{con.}}, \tag{5.31}$$

where time variable relabelling has been used to simplify the last term and terms odd in $\hat{V}^+/\hat{V}^-$ have been ignored, as they will be zero. At first glance it may appear we have a non-zero ‘cross term’ involving both $\hat{V}^+$ and $\hat{V}^-$, but as the $+$ and $-$ operators are effectively independent it will in fact result in a disconnected diagram similar in form to
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Fig. 5.3 and as such can be neglected. Thus

$$U_4 = \frac{1}{4!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \int_0^\beta d\tau_4 \langle T_0 \hat{V}^+(\tau_1) \hat{V}^+(\tau_2) \hat{V}^+(\tau_3) \hat{V}^+(\tau_4) + \hat{V}^-(\tau_1) \hat{V}^-(\tau_2) \hat{V}^-(\tau_3) \hat{V}^-(\tau_4) \rangle,$$

so

$$U_4 = U_4^+ + U_4^-,$$

with connected Feynman diagrams given by Fig. 5.9, and where

$$U_{4}^{\pm} = \beta \sum_{k} |\Delta_{k}^{\pm}| \frac{\text{sech}^2 \left( \frac{\beta \xi_k}{2} \right) (\xi_k^{\pm} \beta - \sinh(\xi_k^{\pm} \beta))}{32 \xi_k^{\pm^3}}.$$  

Again note that this looks like half of our previous $U_4$, so $|l_k| = 0$ returns eq. 5.15.

![Figure 5.9: Connected Feynman diagram for $U_4^\pm$](image)

We now have $U_2$ and $U_4$, and are ready to convert back into the $t/s$ basis. First, we will define

$$\alpha_{\pm} = \frac{\tanh \left( \frac{\beta \xi_k}{2} \right)}{4 \xi_k^{\pm}}$$

and

$$\beta_{\pm} = \frac{\text{sech}^2 \left( \frac{\beta \xi_k}{2} \right) (\xi_k^{\pm} \beta - \sinh(\xi_k^{\pm} \beta))}{32 \xi_k^{\pm^3}}.$$  

Note that both of these are dependent on $k$. Our free energy per particle is now

$$\Omega = \Omega_0 + \frac{1}{V_s} |\Delta_s|^2 + \frac{1}{V_t} |\Delta_t|^2 + \frac{1}{N} \sum_{k} \alpha_+ |\Delta_k^{+}|^2 + \alpha_- |\Delta_k^{-}|^2 + \beta_+ |\Delta_k^{+}|^4 + \beta_- |\Delta_k^{-}|^4,$$

and expanding $\Delta_k^{\pm}$ to $\Delta_s \pm |l_k| \Delta_t$, we find

$$\frac{1}{N} \Omega = \frac{1}{N} \Omega_0 + \alpha_s |\Delta_s|^2 + \alpha_t |\Delta_t|^2 + \beta_s |\Delta_s|^2 + \beta_t |\Delta_t|^4 + (\alpha_{ts} + \beta_{st} |\Delta_s|^2 + \beta_{ts} |\Delta_t|^2)(\Delta_t \Delta_s^{*} + \Delta_s^{*} \Delta_t) + \gamma_1 |\Delta_s|^2 |\Delta_t|^2 + \gamma_2 (\Delta_s^{2} \Delta_t^{*} + \Delta_s^{* 2} \Delta_t),$$

(5.37)
for

\[
\alpha_s = \frac{1}{V_s} + \frac{1}{N} \sum_k \alpha_+ + \alpha_-, \quad (5.38)
\]

\[
\alpha_t = \frac{1}{V_t} + \frac{1}{N} \sum_k |l_k|^2 \alpha_+ + |l_k|^2 \alpha_-, \quad (5.39)
\]

\[
\beta_s = \frac{1}{N} \sum_k \beta_+ + \beta_-, \quad (5.40)
\]

\[
\beta_t = \frac{1}{N} \sum_k |l_k|^4 \beta_+ + |l_k|^4 \beta_-, \quad (5.41)
\]

\[
\gamma_1 = \frac{4}{N} \sum_k |l_k|^2 \beta_+ + |l_k|^2 \beta_-, \quad (5.42)
\]

\[
\gamma_2 = \frac{1}{N} \sum_k |l_k|^2 \beta_+ + |l_k|^2 \beta_-, \quad (5.43)
\]

\[
\alpha_{ts} = \frac{1}{N} \sum_k |l_k| \alpha_+ - |l_k| \alpha_-, \quad (5.44)
\]

\[
\beta_{st} = \frac{1}{N} \sum_k 2 |l_k|(\beta_+ - \beta_-), \quad (5.45)
\]

\[
\beta_{ts} = \frac{1}{N} \sum_k 2 |l_k|^3 (\beta_+ - \beta_-); \quad (5.46)
\]

almost exactly the same as the non-centrosymmetric bulk free energy described in Chapter 4, down to the negative second-order interaction term (here \(\alpha_{ts}\) instead of \(\alpha_{ds}\)). The only difference is the addition of the fourth-order \(\Delta\)-mixing constants \(\beta_{ts}\) and \(\beta_{st}\).

### 5.2.2 Computational Work

We are at last in a position to begin evaluating our model; Fig. 5.10 shows the predicted \(\alpha_s\) and \(\alpha_t\), while Fig. 5.11 shows \(\beta_s\) and \(\beta_t\). These are not significantly affected by the magnitude of \(\lambda\), but a non-zero \(\lambda\)-value not only makes both order parameters appear together as opposed to one appearing alone - it also increases \(T_c\) (see Figs. 5.12a and 5.12b). This is a dramatic impact on the order parameter expression without much change in the \(\alpha_{s/t}\) and \(\beta_{s/t}\) values - what’s going on?

The answer lies in the effect of \(\lambda\) on \(\alpha_{ts}\). When \(\lambda = 0\), \(\xi^+_k = \xi^-_k\) so \(\alpha_+ = \alpha_-\), \(\beta_+ = \beta_-\), and thus \(\alpha_{ts}\), \(\beta_{st}\), and \(\beta_{ts}\) will be zero. Thus the interaction between the order parameters will be identical to that described in the previous chapter - dominated by \(\gamma_1\) and \(\gamma_2\), resulting in the suppression of whichever order parameter has a higher bulk free energy. When \(\lambda \neq 0\), the coefficient \(\alpha_{ts} \neq 0\) and it becomes energetically preferable for both order parameters to appear together. But how can \(T_c\) be so increased, if the point at which \(\alpha_t\) and \(\alpha_s\) become negative isn’t particularly affected by \(\lambda\)?

We can quantify this change to the critical temperature by treating the various terms quadratic in \(\Delta_{s,t}\) as a matrix; we take

\[
\alpha_{\text{matrix}} = \begin{pmatrix} \alpha_s & \alpha_{ts} \\ \alpha_{ts} & \alpha_t \end{pmatrix}, \quad (5.47)
\]
The Bulk Linked Cluster Expansion

Figure 5.10: $\alpha_t$ and $\alpha_s$ vs $k_B T$ for $N = 2000^2$, $V_t = 0.5$, $V_s = 0.468$, $\mu = 0.3$, and $\lambda = 0.09$. $k_B T$ is in units of $2t$. The inset shows the range close to $T_c \approx 5.5 e^{-3}$ in greater detail. A line at 0 on the $y$-axis has been added to enable the discernment of $T_c$. $\lambda = 0$ gives near-identical results. Both $\alpha_s$ and $\alpha_t$ are in units of $1/2t$.

and diagonalize it by finding the eigenvalues $\alpha_1, \alpha_2$ via the usual process:

$$\alpha_{1,2} = \frac{\alpha_s + \alpha_t}{2} \pm \frac{1}{2} \sqrt{(\alpha_s - \alpha_t)^2 + 4\alpha_{ts}}.$$  (5.48)

Note that $\min(\alpha_{1,2}) \leq \min(\alpha_{t,s})$; in the $\lambda = 0$ case $\alpha_{ts} = 0$ and $\alpha_{1,2} = \alpha_{t,s}$, giving the behaviour seen in Fig. 5.12a. In performing this diagonalization we are essentially re-expressing our system in terms of two new order parameters $\eta_{1,2}$, with corresponding second-order constants $\alpha_{1,2}$. The fourth-order coupling terms will be more complex, but fortunately they do not determine the critical temperature and can thus be ignored for our purposes. The order parameters $\eta_{1,2}$ are linear combinations of $\Delta_t$ and $\Delta_s$, so if either $\alpha_1$ or $\alpha_2$ is negative (though $\alpha_1$ will be negative first, due to the inclusion of the $-$ sign) $\Delta_t$ and $\Delta_s$ will appear simultaneously.

In Fig. 5.13, $\alpha_1$ has been plotted alongside the order parameters and the relationship can be seen directly. The subsequent decline of $\Delta_t$ even as $\Delta_s$ continues to increase can be understood by isolating the terms quadratic in $\Delta_t$, creating an ‘effective $\alpha_t$’ similar to eq. 4.29:

$$\alpha_{t}^{eff} |\Delta_t|^2 = (\alpha_t + [\gamma_1 + 2\gamma_2]|\Delta_s|^2)|\Delta_t|^2$$  (5.49)

(the fact that the calculated phase difference of our system is 0 means that there is a $+$ in front of $\gamma_2$ this time). The smaller this is, the lower the free energy cost associated with a non-zero $\Delta_t$ is. This ‘effective $\alpha_t$’ has been plotted alongside $|\Delta_t|$ in Fig. 5.14 and we can observe that it increases dramatically as $|\Delta_s|$ does, resulting in a suppression of $\Delta_t$.

It is now time to begin looking for evidence of TRSB.
5.2.3 Time-Reversal Symmetry Breaking

We can now calculate all of the bulk G-L parameters of our system, and as such are able to seek bulk TRSB with confidence. Wang and Fu predict the occurrence of bulk TRSB only in a small ‘wedge’ in between areas dominated by $\Delta_s$ and $\Delta_t$ [64], and happily we are in a position to check their prediction. We will do this by plotting the phase difference between the order parameters against the $V_t/V_s$ ratio and temperature.

The results for the centrosymmetric and non-centrosymmetric (zero and non-zero $\lambda$) cases are given in Figs. 5.15 and 5.16, and largely agree with Wang and Fu [64]. Because of the effect of $\gamma_2$ and the $\lambda$ dependence of $\alpha_{ts}$, $\lambda = 0$ means that the only possible phase difference between the order parameters is $\phi = \pi/2$, which occurs whenever the two parameters appear together. Interestingly, Fig. 5.15 indicates that even without $\alpha_{ts}$ it is possible for the order parameters to coexist in the bulk - though only for a very specific balance of $k_B T$ and $V_t/V_s$. The inclusion of $\lambda$ (and thus $\alpha_{ts}$) allows for a greater range of phase differences, but it also seems to round the top of the phase ‘wedge’ and move it to the right - in variable terms, to greater $V_t/V_s$ ratios. We also find something a little paradoxical: though $\lambda \neq 0$ increases $T_c$, it seems to slightly decrease the temperature at which Time-Reversal symmetry can be broken. Again, this agrees with Wang and Fu’s predictions [64].

But perhaps the most interesting thing about our phase ‘wedges’ is that there appears in the $\lambda = 0$ case to be a very abrupt phase transition to TRSB at a specific potential ratio - this can be seen in the straight left-hand boundary of the wedge in Fig. 5.15. This boundary can be quantified to some degree by considering the $|\Delta_t|^2$ parts of the free energy, and once again defining an ‘effective $\alpha_t$’:

$$\alpha_t^{eff} |\Delta_t|^2 = (\alpha_t + [\gamma_1 - 2\gamma_2] |\Delta_s|^2) |\Delta_t|^2$$
The Bulk Linked Cluster Expansion

Figure 5.12: $\Delta_t$ and $\Delta_s$ vs $k_B T$ for $N = 2000^2$, $V_s = 0.5$, $V_t = 0.468$, $\mu = 0.3$, and different $\lambda$ values. $k_B T$ and $\Delta$ values are in units of $2t$.

Figure 5.12: $\Delta_t$ and $\Delta_s$ vs $k_B T$ for $N = 2000^2$, $V_s = 0.5$, $V_t = 0.468$, $\mu = 0.3$, and different $\lambda$ values. $k_B T$ and $\Delta$ values are in units of $2t$.

(a) $\lambda = 0$.

(b) $\lambda = 0.09$.

(5.50)

$\alpha_t = (\gamma_1 - 2\gamma_2) \frac{\alpha_s}{2\beta_s}.

(5.51)

$\alpha_s = (\gamma_1 - 2\gamma_2) \frac{\alpha_t}{2\beta_t}.

As we can see from Fig. 5.17 when combined these conditions give the shape of the phase wedge in Fig. 5.15. But what of the non-centrosymmetric case ($\lambda \neq 0$)? We cannot rely on the techniques we have just used, as for $\alpha_{ts} \neq 0$ if one order parameter appears then the other must as well. We instead start by considering the parts of the free energy that are sensitive to the phase difference:

$\gamma_2(\Delta_t^2 \Delta_s^2 + \Delta_t^2 \Delta_s^2) + \alpha_{ts}(\Delta_t \Delta_s^2 + \Delta_t^2 \Delta_s) = 2\gamma_2|\Delta_t|^2|\Delta_s|^2 \cos(2\phi) + 2\alpha_{ts}|\Delta_t||\Delta_s| \cos(\phi),

where we have used the identity $e^{ix} + e^{-ix} = 2 \cos(x)$, and where $\phi$ is the phase difference $\phi_t - \phi_s$. We now take the fourth-order Taylor expansion of the cosines to obtain:

$2|\Delta_t||\Delta_s|\alpha_{ts}(1 - \frac{1}{2} \phi^2 + \frac{1}{24} \phi^4) + 2|\Delta_t|^2|\Delta_s|^2 \gamma_2(1 - 2\phi^2 + \frac{2}{3} \phi^4),

(5.52)

and rearranging this expression into the form

$C_1 \phi^2 + C_2 \phi^4 + C_3,$

we find

$C_1 = -(\alpha_{ts}|\Delta_t||\Delta_s| + 4\gamma_2|\Delta_t|^2|\Delta_s|^2).

(5.53)

For a non-zero $\phi$ to be energetically preferable, $C_1$ must be negative. We therefore set

This differs from the previous $\alpha_{eff}$ because we are dealing with the centrosymmetric system so the phase difference will be $\frac{\pi}{2}$, giving a $-$ sign in front of $\gamma_2$. The ‘critical point’ at which $\Delta_t$ will appear is at $\alpha_{t(eff)} = 0$. In the absence of $\Delta_t$, we can assume that $\Delta_s$ will take its bulk value of $\frac{|\alpha_s|}{2\beta_s}$, allowing us to write the ‘Left-Hand Side’ condition (when $\lambda = 0$) as

$\alpha_t = (\gamma_1 - 2\gamma_2) \frac{\alpha_s}{2\beta_s}.

(5.50)

We can make the same argument for the right-hand side of the phase wedge, giving the ‘Right-Hand Side’ condition

$\alpha_s = (\gamma_1 - 2\gamma_2) \frac{\alpha_t}{2\beta_t}.

(5.51)

As we can see from Fig. 5.17 when combined these conditions give the shape of the phase wedge in Fig. 5.15. But what of the non-centrosymmetric case ($\lambda \neq 0$)? We cannot rely on the techniques we have just used, as for $\alpha_{ts} \neq 0$ if one order parameter appears then the other must as well. We instead start by considering the parts of the free energy that are sensitive to the phase difference:

$\gamma_2(\Delta_t^2 \Delta_s^2 + \Delta_t^2 \Delta_s^2) + \alpha_{ts}(\Delta_t \Delta_s^2 + \Delta_t^2 \Delta_s) = 2\gamma_2|\Delta_t|^2|\Delta_s|^2 \cos(2\phi) + 2\alpha_{ts}|\Delta_t||\Delta_s| \cos(\phi),

where we have used the identity $e^{ix} + e^{-ix} = 2 \cos(x)$, and where $\phi$ is the phase difference $\phi_t - \phi_s$. We now take the fourth-order Taylor expansion of the cosines to obtain:

$2|\Delta_t||\Delta_s|\alpha_{ts}(1 - \frac{1}{2} \phi^2 + \frac{1}{24} \phi^4) + 2|\Delta_t|^2|\Delta_s|^2 \gamma_2(1 - 2\phi^2 + \frac{2}{3} \phi^4),

(5.52)

and rearranging this expression into the form

$C_1 \phi^2 + C_2 \phi^4 + C_3,$

we find

$C_1 = -(\alpha_{ts}|\Delta_t||\Delta_s| + 4\gamma_2|\Delta_t|^2|\Delta_s|^2).

(5.53)

For a non-zero $\phi$ to be energetically preferable, $C_1$ must be negative. We therefore set
\[ C_1 < 0 \] to obtain the inequality
\[ -\alpha_{ts} |\Delta_t||\Delta_s| < 4\gamma_2 |\Delta_t|^2|\Delta_s|^2, \]
and remembering that \( \alpha_{ts} \) is negative we find the condition for a non-zero \( \phi \) value is
\[ \frac{4\gamma_2}{|\alpha_{ts}|} |\Delta_t||\Delta_s| - 1 > 0. \] (5.54)

This is a perfect predictor of phase appearance for our current system, but unfortunately applying it requires calculating \( |\Delta_s| \) and \( |\Delta_t| \), so in general it will usually be better to simply calculate the order parameters and take their phase difference in the usual way. Nevertheless, this condition for a non-trivial phase difference will be very useful later.

This bulk analysis of both \( \lambda = 0 \) and \( \lambda \neq 0 \) systems largely agrees with Wang and Fu’s predictions, and reveals that while TRSB is accessible for physical systems, it is - at least in the bulk - only attainable in a very small region of the phase diagram. However, we have not yet calculated the G-L gradient terms. These will allow us to simulate boundary suppression in our superconductors, and thereby to examine the possibility of a TRSB state occurring at the surface.
Figure 5.14: $\Delta_t$ and $\alpha_t^{\text{eff}}$ vs $k_B T$ for $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0.09$. $k_B T$ and $\Delta$ values are in units of $2t$.

Figure 5.15: $\phi_{\text{diff.}}$ vs $k_B T$ and $V_t/V_s$ for $N = 2000^2, V_s = 0.5, \mu = 0.3, \lambda = 0$, and $V_t$ varied. The white area indicates the non-superconducting regime. $k_B T$ is in units of $2t$. 
Figure 5.16: $\phi_{d.f.}$ vs $k_B T$ and $V_t/V_s$ for $N = 2000^2$, $V_s = 0.5$, $\mu = 0.3$, $\lambda = 0.09$, and $V_t$ varied. The white area indicates the non-superconducting regime. $k_B T$ is in units of $2t$.

Figure 5.17: Left-Hand (red) and Right-Hand (light blue) side conditions overlaid onto Fig. 5.15.
In the previous chapter we were introduced to the Linked Cluster Expansion, and found that it could connect the microscopic Bogoliubov Hamiltonian to the macroscopic uniform Ginzburg-Landau free energy. Using the insight provided by this connection, we analyzed the bulk superconducting state of a superconductor containing singlet and triplet Cooper pairs both with and without inversion symmetry breaking (and thus spin-orbit coupling). In both cases, a Time-Reversal symmetry breaking coexistence of the two order parameters occurred only in a relatively small ‘wedge’ of the parameter space $V_t/V_s$ vs. temperature.

However, we still have yet to include the G-L gradient terms required to account for spatial variation in our superconductor. In order to do so, we will have to allow for a non-zero centre of mass $q$ of the Cooper pairs. This comes from the change from $\Delta$ to $\Delta(r)$ - if $\Delta$ has an $r$-dependence, then it gives rise to a $q$-dependence in momentum space.

For the spatially-varying order parameter $\Delta(r)$ and an operator that destroys an electron with spin $\sigma$ at $r$ $\psi_\sigma(r)$, we use

$$\psi_\sigma(r) = \frac{1}{\sqrt{N}} \sum_k C_{kr} e^{i k \cdot r}, \quad (6.1)$$

and

$$\frac{1}{N} \int dr \Delta(r) e^{-i k \cdot r} = \Delta(k), \quad (6.2)$$

to find

$$\int dr \Delta(r) \psi^\dagger(r) \psi_\downarrow(r) = \frac{1}{N} \sum_{k,k'} C_{k\uparrow} C_{k'\downarrow} \int dr \Delta(r) e^{i (k+k') \cdot r}. \quad (6.3)$$

Setting

$$k = \tilde{k} + \frac{q}{2},$$
$$k' = -\tilde{k} + \frac{q}{2} \quad (6.4)$$

gives

$$\int dr \Delta(r) \psi^\dagger(r) \psi_\downarrow(r) = \frac{1}{N} \sum_{k,q} C_{k+\frac{q}{2}\uparrow} C_{-k+\frac{q}{2}\downarrow} \Delta(q), \quad (6.5)$$

and thus we require the inclusion of $q$ in our calculations.
6.1 Analytic Work

With the inclusion of this $q$, $\hat{V}$ is

$$\hat{V} = \frac{1}{2} \sum_{k,q} \left[ \Delta_+ (q) \left( C_{k+\frac{q}{2} \uparrow} C_{k+\frac{q}{2} \downarrow} - \Uparrow_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} \right) \right. $$

$$+ \Delta_- (q) \left( C_{-k+\frac{q}{2} \uparrow} C_{k+\frac{q}{2} \uparrow} - C_{-k+\frac{q}{2} \downarrow} C_{k+\frac{q}{2} \downarrow} \right) $$

$$+ \Delta_x (q) \left( l_k C_{k+\frac{q}{2} \uparrow} C_{k+\frac{q}{2} \downarrow} - l_k \Uparrow_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} \right) $$

$$+ \Delta_y (q) \left( l_k \Uparrow_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} - l_k C_{-k+\frac{q}{2} \uparrow} C_{k+\frac{q}{2} \downarrow} \right) \right]. \tag{6.6}$$

Note that we have not included a $q$-dependence in $l_k$ here, but the instances of $l_k$ that occur as part of $u$ and $v$ do depend on $q$. Following the argument of Dahl and Sudbø, we assume that the spatial variation is sufficiently weak so as not to change the relative motion of the electrons in Cooper pairs but only modulate $\Delta_{x,y}$ \[65\]. We now apply a slightly more complicated version the transformations from the previous chapter:

$$\left( \begin{array}{cc} C_{\pm k+\frac{q}{2} \uparrow} \\ C_{\pm k+\frac{q}{2} \downarrow} \end{array} \right) = \left( \begin{array}{cc} u_{\pm k+\frac{q}{2}} & v_{\pm k+\frac{q}{2}} \\ -v_{\pm k+\frac{q}{2}}^{\ast} & u_{\pm k+\frac{q}{2}}^{\ast} \end{array} \right) \left( \begin{array}{cc} C_{\pm k+\frac{q}{2} \uparrow} \\ C_{\pm k+\frac{q}{2} \downarrow} \end{array} \right),$$

and their hermitian conjugates, where

$$u_{\pm k+\frac{q}{2}} = \frac{1}{\sqrt{2}} \tag{6.7}$$

and

$$v_{\pm k+\frac{q}{2}} = \frac{1}{\sqrt{2}|l_{\pm k+\frac{q}{2}}|} \left[ \sin \left( \left[ \pm k_y + \frac{q_y}{2} \right] a \right) - i \sin \left( \left[ \pm k_x + \frac{q_x}{2} \right] a \right) \right], \tag{6.8}$$

for

$$|l_{\pm k+\frac{q}{2}}| = \sqrt{\sin \left( \left[ \pm k_y + \frac{q_y}{2} \right] a \right)^2 + \sin \left( \left[ \pm k_x + \frac{q_x}{2} \right] a \right)^2}. \tag{6.9}$$

Expressing $\hat{V}$ in terms of the $+$ and $-$ operators and rearranging, we obtain new ‘cross terms’ $\Delta_{x,y}$ that mix the $+$ and $-$ helicities:

$$\hat{V} = \frac{1}{2} \left[ \Delta_+ (k, q) C_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \uparrow} + \Delta_- (k, q) C_{k+\frac{q}{2} \downarrow} \Uparrow_{k+\frac{q}{2} \downarrow} \right.$$ \n
$$+ \Delta_x (k, q) C_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} + \Delta_x (k, q) C_{k+\frac{q}{2} \downarrow} \Uparrow_{k+\frac{q}{2} \uparrow} \right.$$ \n
$$+ \Delta^+_x (k, q) C_{-k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} + \Delta^-_x (k, q) C_{-k+\frac{q}{2} \downarrow} \Uparrow_{k+\frac{q}{2} \uparrow} \right.$$ \n
$$+ \Delta^+_x (k, q) C_{k+\frac{q}{2} \downarrow} \Uparrow_{k+\frac{q}{2} \uparrow} + \Delta^-_x (k, q) C_{k+\frac{q}{2} \uparrow} \Uparrow_{k+\frac{q}{2} \downarrow} \right] \tag{6.10}$$

with $\Delta_+, \Delta_-, \Delta_x$, and $\Delta^\pm_x$ being given by equations 6.11-6.14:

$$\Delta_+ (k, q) = \Delta_\Uparrow (q) \left( v_{k+\frac{q}{2} \uparrow} u_{k+\frac{q}{2} \downarrow} - u_{k+\frac{q}{2} \uparrow} v_{k+\frac{q}{2} \downarrow} \right) \tag{6.11}$$

$$+ \Delta_\Uparrow (q) \left( \sin(k_y a) - i \sin(k_x a) \right) u_{k+\frac{q}{2} \uparrow} u_{k+\frac{q}{2} \downarrow} - \left( \sin(k_y a) + i \sin(k_x a) \right) v_{k+\frac{q}{2} \uparrow} v_{k+\frac{q}{2} \downarrow} \right).$$

Spatial Variation in the LCE
\[ \Delta_-(k, q) = \Delta_s(q) \left( v_{k+\frac{q}{2}} u_{k+\frac{q}{2}}^* - u_{k+\frac{q}{2}}^* v_{k+\frac{q}{2}} \right) \]  
(6.12)

\[ + \Delta_l(q) \left( [\sin(k_y a) - i \sin(k_x a)] v_{k+\frac{q}{2}} - [\sin(k_y a) + i \sin(k_x a)] u_{k+\frac{q}{2}}^* u_{k+\frac{q}{2}} \right) \]

\[ \Delta_+(k, q) = -\Delta_s(q) \left( v_{k+\frac{q}{2}} u_{k+\frac{q}{2}}^* + u_{k+\frac{q}{2}} v_{k+\frac{q}{2}}^* \right) \]  
(6.13)

\[ - \Delta_l \left( [\sin(k_y a) - i \sin(k_x a)] u_{k+\frac{q}{2}} - [\sin(k_y a) + i \sin(k_x a)] v_{k+\frac{q}{2}}^* u_{k+\frac{q}{2}} \right) \]

\[ \Delta_x(k, q) = \Delta_s(q) \left( u_{k+\frac{q}{2}} u_{k-\frac{q}{2}} + v_{k+\frac{q}{2}} v_{k-\frac{q}{2}}^* \right) \]  
(6.14)

\[ - \Delta_l(q) \left( [\sin(k_y a) - i \sin(k_x a)] u_{k+\frac{q}{2}} u_{k-\frac{q}{2}} + [\sin(k_y a) + i \sin(k_x a)] u_{k+\frac{q}{2}} v_{k-\frac{q}{2}}^* \right) \]

Note that if \( q \to 0 \), the ‘cross terms’ which involve inter-band pairing disappear and we recover the \( \hat{V} \) from the previous chapter. Applying this form of \( \hat{V} \) to \( U_2 \) and taking the parts balanced in \( \pm \) creation and annihilation operators gives

\[ U_2 = \frac{1}{4} \sum_{k,k',q,q'} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \]

\( \alpha(T_+ \Delta_+(k, q) \Delta_+(k', q') C_{k+\frac{q}{2}, \tau}^+ (\tau_1) C_{k-\frac{q}{2}, \tau}^+ (\tau_2) C_{k'+\frac{q}{2}, \tau}^+ (\tau_2) C_{k'-\frac{q}{2}, \tau}^+ (\tau_2) \)

\( + \Delta_- (k, q) \Delta_- (k', q') C_{k+\frac{q}{2}, \tau}^- (\tau_1) C_{k-\frac{q}{2}, \tau}^- (\tau_2) C_{k'-\frac{q}{2}, \tau}^- (\tau_2) C_{k'+\frac{q}{2}, \tau}^- (\tau_2) \)

\( + \Delta_x (k, q) \Delta_x (k', q') C_{k+\frac{q}{2}, \tau}^x (\tau_1) C_{k-\frac{q}{2}, \tau}^x (\tau_2) C_{k'-\frac{q}{2}, \tau}^x (\tau_2) C_{k'+\frac{q}{2}, \tau}^x (\tau_2) \)

\( + \Delta_x (k, q) \Delta_x (k', q') C_{k+\frac{q}{2}, \tau}^x (\tau_1) C_{k-\frac{q}{2}, \tau}^x (\tau_2) C_{k'-\frac{q}{2}, \tau}^x (\tau_2) C_{k'+\frac{q}{2}, \tau}^x (\tau_2) \)

\( + \Delta_x (k, q) \Delta_x (k', q') C_{k+\frac{q}{2}, \tau}^x (\tau_1) C_{k-\frac{q}{2}, \tau}^x (\tau_2) C_{k'-\frac{q}{2}, \tau}^x (\tau_2) C_{k'+\frac{q}{2}, \tau}^x (\tau_2) \)

\( + \Delta_x (k, q) \Delta_x (k', q') C_{k+\frac{q}{2}, \tau}^x (\tau_1) C_{k-\frac{q}{2}, \tau}^x (\tau_2) C_{k'-\frac{q}{2}, \tau}^x (\tau_2) C_{k'+\frac{q}{2}, \tau}^x (\tau_2) \) \text{con.}

with, as usual, basic \( \tau \)-variable relabelling. All of the resultant Wick’s theorem terms require \( q' = q \) to be non-zero, but the \( k \) picture is more nuanced. For the \( \Delta_+ \Delta_+ \) and \( \Delta_- \Delta_- \) parts both \( k' = k \) and \( k' = -k \) give valid (and equal) results, but the \( \Delta_+ \Delta_- \) \( \Delta_- \Delta_+ \) parts require \( k' = k \) in order to give a non-zero result. The \( \Delta_x \Delta_x \) \( \Delta_x \Delta_x \) parts require \( k' = -k \). However, attentive readers will notice from the definitions given above that \( \Delta_x (k \to -k) = -\Delta_x \). This would seem at first to cancel the cross terms, but in fact arranging the creation and annihilation operators into the same order as those terms adds another factor of \(-1\), causing them to add instead. In addition, we can observe that as \( |\Delta_x|^2 (k \to -k) = |\Delta_x|^2 \) and we are summing over a symmetric \( k \)-space, the \( \Delta_x \) and \( \Delta_x \) \( \Delta_x \) \( \Delta_x \) terms will in fact be equivalent (including the operators). Evaluating the trace and integrals, can write \( U_2 \) as

\[ U_2 = \frac{1}{2} \sum_{k,q} U_2^+ (k, q) + U_2^- (k, q) + U_2^x (k, q) , \]  
(6.16)

where

\[ U_2^\pm (k, q) = |\Delta_\pm|^2 \frac{1}{i \omega_n - \xi_{k+\frac{q}{2}, \pm} - i \omega_n - \xi_{-k+\frac{q}{2}, \pm} } \]

(6.17)
and
\[ U_2^\pm(k,q) = 4|\Delta_x|^2 \frac{1}{i\omega_n - \xi_{k+\frac{q}{2},+}} \frac{1}{i\omega_n - \xi_{-k+\frac{q}{2},-}}. \]  

(6.18)

Similarly to the previous chapter, the normal-state dispersion is \( \xi_{\pm k+\frac{q}{2},\pm} = \xi_{\pm k+\frac{q}{2}} \pm \lambda|l_{\pm k+\frac{q}{2}}|. \) Evaluating the \( \Delta \) terms and substituting in the definition of \( u_k \) gives

\[ |\Delta_+(k,q)|^2 = |\Delta_s(q)|^2 \frac{1}{2} \left[ 1 - 2\Re \left( v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}}^* \right) \right] 
+ |\Delta_t(q)|^2 \frac{1}{2} \left[ (\sin^2(k_y a) + \sin^2(k_x a)) - 2\Re \left( [\sin(k_y a) - i \sin(k_x a)]^2 v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}} \right) \right] + \frac{1}{\sqrt{2}} |\Delta_l(q)| \Delta_s^*(q) + \Delta^*_l(q) \Delta_s(q)|^2 \Re \left( [\sin(k_y a) - i \sin(k_x a)] [v_{k+\frac{q}{2}} - v_{-k+\frac{q}{2}}] \right), \]

(6.19)

\[ |\Delta_-(k,q)|^2 = |\Delta_s(q)|^2 \frac{1}{2} \left[ 1 - 2\Re \left( v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}}^* \right) \right] 
+ |\Delta_t(q)|^2 \frac{1}{2} \left[ (\sin^2(k_y a) + \sin^2(k_x a)) - 2\Re \left( [\sin(k_y a) - i \sin(k_x a)]^2 v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}} \right) \right] - \frac{1}{\sqrt{2}} |\Delta_l(q)| \Delta_s^*(q) + \Delta^*_l(q) \Delta_s(q)|^2 \Re \left( [\sin(k_y a) - i \sin(k_x a)] [v_{k+\frac{q}{2}} - v_{-k+\frac{q}{2}}] \right), \]

(6.20)

and

\[ |\Delta_\times(k,q)|^2 = |\Delta_s(q)|^2 \frac{1}{2} \left[ 1 + 2\Re \left( v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}}^* \right) \right] 
+ |\Delta_t(q)|^2 \frac{1}{2} \left[ (\sin^2(k_y a) + \sin^2(k_x a)) + 2\Re \left( [\sin(k_y a) - i \sin(k_x a)]^2 v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}} \right) \right] + \frac{1}{\sqrt{2}} |\Delta_l(q)| \Delta_s^*(q) + \Delta^*_l(q) \Delta_s(q)|^2 \Re \left( [\sin(k_y a) - i \sin(k_x a)] [v_{k+\frac{q}{2}} + v_{-k+\frac{q}{2}}] \right). \]

(6.21)

The resultant Feynman diagrams are given in Figs. 6.1a and 6.1b.

Figure 6.1: Feynman diagrams for \( U_2^\pm(k,q) \) and \( U_2^\times(k,q) \).

Expanding the \( v_{\pm k+\frac{q}{2}} \) and \( \xi_{\pm k+\frac{q}{2},\pm} \) terms manually in \( q \) is possible, but not particularly time effective. This part of the working was therefore delegated to Wolfram Mathematica. Each expression decomposed with regard to \( q \) using the Series command, and the \( q_x^2, q_y^2 \) and \( q \)-free parts were isolated and simplified with FullSimplify, rendering expressions of the form

\[ U_2^\pm(k,q) = |\Delta_s(q)|^2 \left( \alpha_+ + q_x^2 K_{s,x,+} + q_y^2 K_{s,y,+} \right) 
+ |\Delta_t(q)|^2 \left( |k|^2 \alpha_+ + q_x^2 K_{t,x,+} + q_y^2 K_{t,y,+} \right) + \frac{1}{\sqrt{2}} |\Delta_l(q)| \Delta_s^*(q) + \Delta^*_l(q) \Delta_s(q)| \left( |k|^2 \alpha_+ + q_x^2 K_{l,x,+} + q_y^2 K_{l,y,+} \right). \]

(6.22)

The \( K_{t,x,+} \), etc. terms are the ‘building blocks’ which are summed over \( k \) and then
 combined to create the $K_{(t/s),(x/y)}$ terms - for instance $K_{t,x} = \sum_k K_{t,x,+} + K_{t,x,-} + K_{t,x,x}$. Explicit expressions are not provided for $K_{t,x,+}$, etc. as they are not particularly enlightening and rather long.

The selective isolation is because we are discarding terms above second order in $q$ and expressions odd in $q$ will sum to zero over $k$ [65]. The remaining $q^2_{x,y}$ terms will become partial derivatives when transformed from $q$-space into $r$-space due to the Fourier transform property

$$\Delta(r) = \int \Delta(q) e^{iq \cdot r} dr,$$

which, applying $\partial_{x,y}$ to both sides, gives

$$-i\partial_{x,y}\Delta(r) = \int q_{x,y}\Delta(q) e^{iq_{x,y}r} dr$$

and its complex conjugate.

The resultant $K$, $\alpha$ expressions are then combined and summed from $k_x$, $k_y = -\frac{\pi}{a}$ to $k_x$, $k_y = \frac{\pi}{a}$ using the `NIntegrate` command. The results for the non-gradient terms are identical to those of the MATLAB program developed in the previous chapter, and the gradient terms have the property $K_{(s/t/st),x} = K_{(s/t/st),y}$. This is expected due to the symmetries of the superconducting states. In the system we have been considering - that of a superconductor filling the half-space $x > 0$ - there will be no spatial variation in the $y$-direction, so the G-L free energy contribution from the gradient is

$$F_{\text{grad}} = \int_{0}^{\infty} (K_{s,x} |\partial_x \Delta_s|^2 + K_{t,x} |\partial_x \Delta_t|^2 + K_{ts,x} [(\partial_x \Delta_s)(\partial_x \Delta_t^*) + (\partial_x \Delta_t^*)(\partial_x \Delta_s)]) dx. \quad (6.24)$$

The $y$-gradient terms are nonetheless still valuable, as the presence of the expected symmetries is a useful ‘sanity check’. When $\lambda = 0$, $K_{t,x} = 0$ as well - this is expected due to centrosymmetry preventing second-order interactions between the order parameters. $K_{t,x}$ and $K_{s,x}$ are non-zero for all $\lambda$. We are now ready to minimize the free energy of a spatially inhomogeneous superconductor using our Ginzberg-Landau technique.

### 6.2 Connecting to the Ginzburg-Landau Simulation

We will not be conducting the non-zero $q$ expansion for $l = 4$, as this would be extremely complex and only add higher-order gradient terms that are assumed to be negligibly small. The fourth-order $\Delta$ terms are therefore obtained using the same process described in the previous chapter.

We now have the ability to calculate all of the non-magnetic terms from our G-L free energy, so we can finally replicate the G-L simulations we performed in Chapter 3. We pick a temperature and $V_t/V_s$ that place us in the $\Delta_t$ dominated part of Figs. 5.15 and 5.16 ($k_B T = 0.0045$, $V_t/V_s = 0.917$), and obtain Figs. 6.2 and 6.3.

These results are very much as we expected. In the no spin-orbit coupling case Fig. 6.2 the order parameters appear together only at the surface (as they did in Fig. 4.5), while in the spin-orbit coupling case Fig. 6.3 they coexist in the bulk with $\phi = 0$ but only develop a non-zero phase difference at the surface, as Timm et al. predicted [53]. There is one key surprise in Fig. 6.3: The phase difference between $\Delta_t$ and $\Delta_s$ peaks not at the surface, but around 10 $\xi_t$-lengths away from it. This behaviour is not immediately apparent in Fig. 1.3, but on closer examination we can see that perhaps this phase difference ‘kink’ may show...
Spatial Variation in the LCE

Figure 6.2: $\Delta_t$ and $\Delta_s$ vs $x$ for $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0$ and $k_B T = 0.0045$. $\Delta$ values are in units of $2t$. As expected, the presence of centrosymmetry prevents the order parameters from coexisting in the bulk.

up there too. The real and imaginary parts of the order parameters in Fig. 1.3 are plotted separately, but the imaginary parts of the components of the dominant order parameter ($\Delta^s_{l+1/2}$ and $\Delta^s_{l}$) appear to increase significantly more than that of the sub-dominant order parameter ($\Delta^s_{l}$) in the closest plotted point to the boundary. This would seem to suggest that if the difference between the phases were plotted, it may indeed be at its maximum at some point before the boundary - perhaps very close, as the tight-binding approximation used by Timm et al. requires very small coherence lengths. A revisiting of Timm et al.’s work at a later date is perhaps warranted.

There is still much we can productively do with our own results, however - we will start by trying to analytically determine the phase behaviour of our G-L system. We already derived a condition for a non-zero $\phi$ in the bulk (see eq. 5.54), so why not see what happens if we apply it here? Fig. 6.4 shows that this does predict a phase difference in our system, but of a slightly different shape. Eq. 5.54 predicts a phase difference of zero at the surface, and a much faster $\phi$ decay than we actually observe. What’s going on? The $\gamma_2$ and $\alpha_{ts}$ terms are not the only parts of our free energy expression that determine the phase difference - the gradient terms $|\partial_x \Delta_{t/s}|^2$ also affect the phase, though it is difficult to determine exactly how with analytic tools. It is therefore instructive to examine the problem computationally. By taking the calculated $|\Delta_t|$ and $|\Delta_s|$ values, feeding them into the function

$$2\gamma_2|\Delta_t|^2|\Delta_s|^2 \cos(2\phi) + 2\alpha_{ts}|\Delta_t||\Delta_s| \cos(\phi) \quad (6.25)$$

and minimizing with regard to $\phi$, we can obtain the behaviour of the phase difference without the effects of the gradient terms, essentially making a local approximation of the phase. An example of this technique along with the true non-approximated phase and the condition calculated in eq. 5.54 can be seen in Fig. 6.5.

As we can see, the local approximation results in a higher peak and faster decay than the ‘true’ phase, as well as predicting no phase difference at the surface. Reassuringly it is
only non-zero when the ‘phase condition’ of eq. 5.54 is positive, as we would expect. We can now determine the effects of the gradient terms on the phase difference: they resist rapid changes to the magnitude, ‘evening out’ the shape and resulting in the longer decay that we observed in Fig. 6.4. It seems that the gradient terms are also responsible for the non-zero phase difference we have observed at the superconductor’s boundary - both our ‘TRSB condition’ and the local approximation predict no phase difference at all at the surface, but a rapid jump a little in from the material’s boundary. The gradient terms impose a free energy cost to rapid changes in the relative phase of our order parameters as well as their magnitudes.

The local approximation is still a very good predictor of TRSB, but it is by no means perfect - the ‘evening’ effects of the gradient terms can sometimes result in no phase difference anywhere in the material, even when the local approximation predicts one should arise. This is demonstrated by Figs. 6.7a and 6.7b; a difference of 0.001 in the $V_t/V_s$ ratio is enough to take the system from TRSB to no TRSB. Note that this can occur even when the local approximation predicts a not insignificant value of $\phi$. Despite its imperfection, the local approximation emphasises the mechanism by which we can obtain TRSB near the surface of no bulk-TRSB systems: The suppression of $\Delta_t$ changes the balance of the order parameters, artificially forcing the system into behaving like one in which the $V_t/V_s$ ratio is lower. In the case of the local approximation, which effectively treats each $x$-point as a separate bulk system, this can be thought of as moving to the left on Fig. 5.16 (an illustration of this concept is provided in Fig. 6.6). For some systems, this may be insufficient to produce TRSB, while for others - such as the one explored in Figs. 6.3-6.5 it may move the system from complete $\Delta_t$ domination in the bulk to complete $\Delta_s$ domination close to the surface, resulting in the local approximation predicting no phase difference in both of those areas.

Now that we can calculate the G-L gradient terms of our system and understand their effects on TRSB availability, we can add one final element to the simulation: the magnetic
Figure 6.4: $\Delta_t$, $\Delta_s$, and the ‘TRSB condition’ vs $x$ for $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0.09$ and $k_BT = 0.0045$. $\Delta$ values are in units of $2t$. Some results have been divided by 100 to be visible on the same axes as $\Delta_t/s$. A line at 0 on the $y$-axis has been added to aid reading of the ‘phase condition’. The phase differences and ‘phase condition’ are dimensionless.

order parameter.
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Figure 6.5: $\Delta_t$, $\Delta_s$, $\phi$, the ‘TRSB condition’, and the local phase approximation vs $x$ for $N = 2000^2$, $V_s = 0.5$, $V_t = 0.468$, $\mu = 0.3$, $\lambda = 0.09$ and $k_BT = 0.0045$. $\Delta$ values are in units of $2t$. Some results have been divided by 100 to be visible on the same axes as $\Delta_t/s$. A line at 0 on the $y$-axis has been added to aid reading of the ‘phase condition’. The phase differences and ‘phase condition’ are dimensionless.

Figure 6.6: An illustration of the effects of $\Delta_t$ suppression on our system in terms of the bulk solutions. The bulk plot was calculated with the same parameters as Fig. 5.16. This figure is for illustration purposes only, and the positions of the ‘surface’ and ‘bulk’ points are not based on any particular case.
Figure 6.7: $\Delta_t$, $\Delta_s$, and the local phase approximation vs $x$ for $N = 2000^2$, $V_s = 0.5$, $\mu = 0.3$, $\lambda = 0.09$, $k_B T = 0.0045$, and $V_t$ varied. $\Delta$ values are in units of $2t$. Some results have been divided by 100 to be visible on the same axes as $\Delta_t/s$. The phase differences are dimensionless.
In the previous chapter we calculated the G-L gradient terms by incorporating a non-zero centre of mass of the Cooper pairs \( q \) into the Bogoliubov Hamiltonian. This allowed us to simulate spatially inhomogeneous superconductors, and we found that it is possible for the scenario described by Timm et al. to occur. We went on to use the bulk ‘TRSB condition’ from Chapter 5 and develop a ‘local approximation’ for the phase, both of which added to our understanding of the system. We finally acknowledged that this is not quite enough to pronounce our investigation a success - we must include the possibility of a non-zero magnetic order parameter to have full confidence in our results.

In this chapter, we will add a magnetic term to the Bogoliubov Hamiltonian and use the Linked Cluster Expansion to obtain the coupling between the magnetic and superconducting order parameters in our Ginzburg-Landau free energy. This will allow us to test whether such an order parameter does in fact arise, and gauge its effect on the system if it does. In contrast to Chapter 4, we will consider coupling to a spin polarization of the electrons; the conditions for a direct coupling to the vector potential are not satisfied in our system.

### 7.1 Modifying the Hamiltonian

Adding a magnetic component to the system means adding a Zeeman-type magnetic coupling term to the Hamiltonian, which has the form

\[
\hat{V}_M = \sum_{k,i,j} C_{ki}(\vec{M} \cdot \vec{\sigma})_{ij} C_{kj},
\]

where \( i \) and \( j \) denote spin indices and \( \vec{M} = (M_x, M_y, M_z) \), so

\[
\vec{M} \cdot \vec{\sigma} = \begin{bmatrix} M_z & M_x - iM_y \\ M_x + iM_y & -M_z \end{bmatrix}.
\]

Applying the transformation into the helicity basis from the previous chapter to this results in a total M-term of

\[
\hat{V}_M = \sum_{k,q} M_{+k+q} + M_{+k+q}^\dagger + M_{k+q} + M_{-k+q}^\dagger,
\]
where

\[ M_{\pm k + \frac{\bar{q}}{2}} = 2M_x u_{\pm k + \frac{\bar{q}}{2}} v^*_{\pm k + \frac{\bar{q}}{2}} C^\dagger_{\pm k + \frac{\bar{q}}{2}, \tau} + M_y \times \]

\[ \left( v^*_{\pm k + \frac{\bar{q}}{2}} u_{\pm k + \frac{\bar{q}}{2}} C_{\pm k + \frac{\bar{q}}{2}, \tau} + C_{\pm k + \frac{\bar{q}}{2}, \tau}^\dagger \right) \]

\[ + u^*_{\pm k + \frac{\bar{q}}{2}} v_{\pm k + \frac{\bar{q}}{2}} C_{\pm k + \frac{\bar{q}}{2}, \tau} + v^*_{\pm k + \frac{\bar{q}}{2}} C_{\pm k + \frac{\bar{q}}{2}, \tau}^\dagger \right). \tag{7.4} \]

Note that \( \hat{V}_M \) is its own Hermitian conjugate, and is symmetric in \( k \). Also note that in contrast to the \( \Delta \) terms we have been dealing with up to this point, \( \hat{V}_M \) has creation and annihilation operators appearing together rather than separately - these properties will be useful later. We will be performing expansions up to second order in M. As the ground state of the non-interacting Hamiltonian is not spin-polarised the \( U_1 \) term will be zero, so we start with the \( U_2 \) term:

### 7.1.1 The Second-order Term

As each part of \( \hat{V}_M \) contains one creation and one annihilation operator, a second-order product such as \( \hat{V}_M \hat{V} \) will have an non-equal number of each. They will thus be zero, leaving the only non-zero magnetic part of \( U_2 \) as

\[ U_2(M) = \frac{1}{2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \langle 0 | T_\tau \hat{V}_M(\tau_1) \hat{V}_M(\tau_2) | 0 \rangle_{\text{con.}}. \tag{7.5} \]

With \( \tau \) and \( k \) re-labelling, we can write \( \langle 0 | T_\tau \hat{V}_M(\tau_1) \hat{V}_M(\tau_2) | 0 \rangle \) as

\[ 4 \sum_{k, \bar{q}} \left[ \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}(\tau_1) M_{+ k + \frac{\bar{q}}{2}}(\tau_2) | 0 \rangle + \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_1) M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_2) \rangle \right. \]

\[ \left. + 2 \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_1) M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_2) \rangle \right], \tag{7.6} \]

recalling that we are summing \( k \) over an even area so \( \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}(\tau_1) M_{+ k + \frac{\bar{q}}{2}}(\tau_2) \rangle = \langle 0 | T_\tau M_{- k - \frac{\bar{q}}{2}}(\tau_1) M_{- k - \frac{\bar{q}}{2}}(\tau_2) \rangle \). Any \( \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}} M_{- k + \frac{\bar{q}}{2}} \rangle \) terms will be zero as we are taking only connected diagrams, and Wick’s theorem ensures that \( \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}} M_{+ k + \frac{\bar{q}}{2}} \rangle \) will be zero for \( \bar{q} \neq q \).

We now examine the individual non-zero connected-diagram parts of this expression, and substituting in \( u_k = \frac{1}{\sqrt{2}} \) we find

\[ \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}(\tau_1) M_{+ k + \frac{\bar{q}}{2}}(\tau_2) \rangle = \]

\[ \sqrt{2} M_x (M_x - M_y) u^*_{\pm k + \frac{\bar{q}}{2}} G^+ (+ k + \frac{\bar{q}}{2}, \tau_1 - \tau_2) G^- (+ k + \frac{\bar{q}}{2}, \tau_2 - \tau_1) \]

\[ + \frac{1}{2} (M_x - M_y)^2 u^*_{\pm k + \frac{\bar{q}}{2}} [2 G^+ (+ k + \frac{\bar{q}}{2}, \tau_1 - \tau_2) G^- (+ k + \frac{\bar{q}}{2}, \tau_2 - \tau_1) \]

\[ - G^+ (+ k + \frac{\bar{q}}{2}, \tau_1 - \tau_2) G^+ (+ k + \frac{\bar{q}}{2}, \tau_2 - \tau_1) - G^- (+ k + \frac{\bar{q}}{2}, \tau_1 - \tau_2) G^- (+ k + \frac{\bar{q}}{2}, \tau_2 - \tau_1) \], \tag{7.7}

while

\[ \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_1) M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_2) \rangle = \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \langle 0 | T_\tau M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_1) M_{+ k + \frac{\bar{q}}{2}}^\dagger(\tau_2) \rangle^*, \]
and

\[2\phi(T_\tau M_{+k+\frac{q}{2}}(\tau_1), M_{+k+\frac{q}{2}}(\tau_2)) = -2M^2G^+(+k + \frac{q}{2}, \tau_1 - \tau_2)G^-(+k + \frac{q}{2}, \tau_2 - \tau_1) - 2\sqrt{2}\Re[M_z(M_x - iM_y)v^+_{k+\frac{q}{2}}]G^+(+k + \frac{q}{2}, \tau_1 - \tau_2)G^-(+k + \frac{q}{2}, \tau_2 - \tau_1)
- \frac{1}{2}(M_z^2 + M_y^2)[2G^+(+k + \frac{q}{2}, \tau_1 - \tau_2)G^-(+k + \frac{q}{2}, \tau_2 - \tau_1)] + G^-(+k + \frac{q}{2}, \tau_1 - \tau_2)G^+(+k + \frac{q}{2}, \tau_2 - \tau_1)] \tag{7.8}\]

Grouping all of this by Green’s function allows us to write

\[0(T_\tau \hat{V}_M(\tau_1) \hat{V}_M(\tau_2)) = -G^+(+k + \frac{q}{2}, \tau_1 - \tau_2)G^-(+k + \frac{q}{2}, \tau_2 - \tau_1) \times \left(4\sqrt{2}\Re[M_z(M_x - iM_y)v^+_{k+\frac{q}{2}}] - 2\Re([M_z - iM_y]v^2_{k+\frac{q}{2}}) + 2M^2_z + M^2_y\right) \tag{7.9}\]

\[\times \left[G^+(+k + \frac{q}{2}, \tau_1 - \tau_2)G^+(+k + \frac{q}{2}, \tau_2 - \tau_1) + G^-(+k + \frac{q}{2}, \tau_1 - \tau_2)G^-(+k + \frac{q}{2}, \tau_2 - \tau_1)\right] \times \left(\Re[(M_x - iM_y)^2v^2_{k+\frac{q}{2}}] + \frac{1}{2}(M^2_x + M^2_y)\right).\]

We then perform a decomposition in \(q\), just like the previous chapter. Out of the constants attending the 54 resultant \(M-q\) pairings in \(U_2\) (\(Mx^2q^2_x, M^2_yq_y\), etc.), only twelve integrate to a non-zero value. In G-L terms, these would contribute

\[\int [(K_x M_x^2 + K_y M_y^2 + K_y M_y^2 + K_y M_y^2 + K_x M_x^2 + K_x M_x^2 + K_x M_x^2 + K_x M_x^2 + K_x M_x^2) +\]
\[+ (K_{xy} M_x \partial_x M_x + M_x \partial_x M_x + \partial_x M_x) + (\partial_y M_y) \partial_y M_x + [\partial_y M_y] \partial_y M_x + [\partial_y M_x] \partial_y M_y] dxdy \tag{7.10}\]

to the free energy, with the symmetries

\[K_x = K_y, \]
\[K_{xy} = K_{yx}, \]
\[K_{yx} = K_{xy}, \]
\[K_{xx} = K_{yy}, \]
\[K_{zxy} = -K_{xyz}. \tag{7.11}\]

The terms that include derivatives are larger than the non-derivative terms, but not significantly enough - as we expect the magnetic order parameter to be very small, its gradient will be even smaller. We will thus only use the non-gradient terms \(K_x, K_y, K_z\) from this expression in our G-L free energy.

### 7.1.2 The Third-order Term

It is in \(U_3\) that we can first obtain a \(\Delta-M\) coupling term, which with basic \(\tau\)-switching we can write

\[U_3(M) = -\frac{1}{6} \int_0^3 d\tau_1 \int_0^3 d\tau_2 \int_0^3 d\tau_3 0(3\hat{V}_M(\tau_1)\hat{V}(\tau_2)\hat{V}(\tau_3))_{con.} \tag{7.12}\]
(V₂⁺V terms will be zero as they will have unequal numbers of creation and annihilation operators, and the V₃⁻ term will also be zero due to the absence of spin-polarization in the ground state). V is the same as in the previous chapter, and with knowledge of the Δₓ, Δₓ̂ equivalence can be written V = Vₓ + Vₙ + 2Vₓ̂, where

\[ \hat{V}_x = \frac{1}{2} \sum_{k,q} \left[ \Delta_+(k, q) C_{k+q, q}^+ C_{-k+q, q}^+ + \Delta^*_+(k, q) C_{-k+q, q}^+ C_{k+q, q}^+ \right], \quad (7.13) \]

\[ \hat{V}_n = \frac{1}{2} \sum_{k,q} \left[ \Delta_-(k, q) C_{k+q, q}^+ C_{-k+q, q}^+ + \Delta^*_-(k, q) C_{-k+q, q}^+ C_{k+q, q}^+ \right], \quad (7.14) \]

and

\[ \hat{V}_x = \frac{1}{2} \sum_{k,q} \left[ \Delta_x(k, q) C_{k+q, q}^+ C_{-k+q, q}^+ + \Delta^*_x(k, q) C_{-k+q, q}^+ C_{k+q, q}^+ \right], \quad (7.15) \]

for the same Δₚ,ₓ given by eqs. 6.11 to 6.14.

Expanding the V terms in eq. 7.12 and taking the Δ pairings that can form non-zero connected diagrams we obtain

\[ U_3 = -2 \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int_0^\beta d\tau_3 \sum_{k,k',k'',q,q',q''} \Delta_+(k, q) \Delta^*_+(k'', q'') M_+(k', q') G^+ \left( k + \frac{q}{2}, \tau_1 - \tau_3 \right) G^+ \left( k' + \frac{q'}{2}, \tau_3 - \tau_2 \right) \times \]

\[ \delta_q q' \delta_q' q'' \delta_{k,k'} \delta_{k,-k''} \]

\[ + \Delta_-(k, q) \Delta^*_-(k'', q'') M_-(k', q') G^- \left( k + \frac{q}{2}, \tau_1 - \tau_3 \right) G^- \left( k' + \frac{q'}{2}, \tau_3 - \tau_2 \right) \times \]

\[ \delta_{q,q'} \delta_{q',q''} \delta_{k,k'} \delta_{k,-k''} \]

\[ + \Delta_x(k, q) \Delta^*_x(k'', q'') M_+ \times (k', q') + \Delta^*_x(k, q) \Delta_+ \times (k'', q'') M_+ \times (k', q') \right) G^+ \left( k + \frac{q}{2}, \tau_1 - \tau_2 \right) \times \]

\[ \delta_{q,q'} \delta_{q',q''} \delta_{k,k'} \delta_{k,-k''} \]

\[ + \Delta_-(k, q) \Delta^*_-(k'', q'') M_- \times (k', q') + \Delta^*_x(k, q) \Delta_+ \times (k'', q'') M_- \times (k', q') \right) G^+ \left( k + \frac{q}{2}, \tau_1 - \tau_2 \right) \times \]

\[ \delta_{q,q'} \delta_{q',q''} \delta_{k,k'} \delta_{k,-k''} \]

for

\[ M_\pm(k', q') = \pm \sqrt{2} \Re \left[ (M_x - i M_y) v_{k'} + \frac{q'}{2} \right], \quad (7.17) \]

\[ M_+ \times (k', q') = \sqrt{2} M_x v_{k'} + \frac{q'}{2} - (M_x - i M_y) v_{k'} + \frac{1}{2} (M_x + i M_y), \quad (7.18) \]

\[ M_- \times (k', q') = \sqrt{2} M_x v_{k'} + \frac{q'}{2} + \frac{1}{2} (M_x - i M_y) - (M_x + i M_y) v_{k'} \quad (7.19) \]

Note that Wick’s theorem has imposed some conditions on the k, k', k'', and q, q', q'' relationships. The |Δ_+|^2 and |Δ_-|^2 terms are relatively straightforward to deal with, as we
already know their non-$M$ parts from the previous chapter (substituting in $u_k = \frac{1}{\sqrt{2}}$):

$$|\Delta_\pm(k, q)|^2 = |\Delta_s(q)|^2 \frac{1}{2} \left[ 1 + 2\Re \left( v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}}^* \right) \right]$$

$$+ |\Delta_t(q)|^2 \frac{1}{2} \left[ (\sin^2(k_y a) + \sin^2(k_x a)) + 2\Re \left( |\sin(k_y a) - i \sin(k_x a)|^2 v_{k+\frac{q}{2}} v_{-k+\frac{q}{2}}^* \right) \right]$$

$$\pm \frac{1}{\sqrt{2}} \left[ |\Delta_t(q)| \Delta_s^*(q) + \Delta_t^*(q) \Delta_s(q) \right] \Re \left( |\sin(k_y a) - i \sin(k_x a)| v_{k+\frac{q}{2}} + v_{-k+\frac{q}{2}}^* \right).$$

The connected Feynman diagrams that result from these terms are given by Fig. 7.1. The connected Feynman diagrams structure for the $|\Delta_\pm|^2$ parts of $U_3$

![Figure 7.1: Connected Feynman diagram structure for the $|\Delta_\pm|^2$ parts of $U_3$](image)

The terms involving $\Delta_\times$ are a little trickier. Adding both of the allowed $k, k', k''$ combinations results in the total expressions (substituting in the identity of $u_k$):

$$\Delta_\times(k, q) \Delta_\times^*(k'', q') M_{+\times}(k', q') + \Delta_\times^*(k, q) \Delta_\times(k'', q') M_{+\times}^*(k', q') =$$

$$4\sqrt{2} \Re \left[ |\Delta_s(q)|^2 \left( v_{k+\frac{q}{2}}^2 v_{-k+\frac{q}{2}} - \frac{1}{2} v_{-k+\frac{q}{2}}^* \right) M_{+\times}(+k, q) \right]$$

$$+ 4\sqrt{2} \Re \left[ |\Delta_t(q)|^2 \left( |\sin(k_y a) + i \sin(k_x a)|^2 \frac{1}{2} v_{-k+\frac{q}{2}}^* \right) M_{+\times}(+k, q) \right]$$

$$- \left[ \Delta_s(q) \Delta_t(q) \left( |\sin(k_y a) - i \sin(k_x a)| v_{k+\frac{q}{2}}^* v_{-k+\frac{q}{2}} - \frac{1}{2} \right) M_{+\times}(+k, q) \right]$$

$$\pm \left[ \Delta_s^*(q) \Delta_t(q) \left( |\sin(k_y a) - i \sin(k_x a)| \frac{1}{2} \right) M_{+\times}(+k, q) \right]$$

(7.21)
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\[ \Delta_-(k, q) \Delta_+^*(k, q) M_{\times x}(-k, q) + \Delta_+^*(k, q) \Delta_\times(k, q) M_{\times x}^*(k, q) = \]

\[ 4\sqrt{2} \Re \left[ |\Delta_+(q)|^2 \left( \frac{1}{2} v_{+k+\frac{2}{2}} - v_{+k+\frac{2}{2}} v_{+k-\frac{2}{2}} \right) M_{\times x}(-k, q) \right] \]

\[ + 4\sqrt{2} \Re \left[ |\Delta_+(q)|^2 \left( [\sin(k_y a) + i \sin(k_x a)]^2 v_{-k+\frac{2}{2}} v_{-k+\frac{2}{2}} \right) M_{\times x}(+k, q) \right] \]

\[ - [\sin(k_y a) - i \sin(k_x a)]^2 \left( \frac{1}{2} v_{+k+\frac{2}{2}} v_{-k+\frac{2}{2}} \right) M_{\times x}(+k, q) \]

\[ - \left[ \Delta_+^*(q) \Delta_\times(q) \left( [\sin(k_y a) - i \sin(k_x a)] \left( \frac{1}{2} - v_{+k+\frac{2}{2}} v_{-k+\frac{2}{2}} \right) \right. \right. \]

\[ + \left. \left. [\sin(k_y a) + i \sin(k_x a)] \left( v_{+k+\frac{2}{2}} v_{-k+\frac{2}{2}} - v_{-k+\frac{2}{2}} v_{+k+\frac{2}{2}} \right) \right) M_{\times x}(-k, q) + c.c. \right] , \]

where we have used c.c. to stand for the complex conjugate of the previous expression.

Readers may well be concerned about the coefficients of the \( \Delta_+^* \Delta_\times \) and \( \Delta_\times \Delta_+^* \) terms given by these expressions - these are not explicitly real, while all of the other terms being integrated to obtain G-L constants are. Fortunately, the imaginary part of these expressions is odd in \( k \) and so integrating them does in fact produce real constants. Examples of Feynman diagrams for the terms involving \( \Delta_\times \) are given by Figs. 7.2 and 7.3. Once everything

\[ \begin{array}{c}
\Delta_+(q) \\
\Delta_\times(q)
\end{array} \]

\[ \begin{array}{c}
\tau_1 \\
\tau_2 \\
\tau_3
\end{array} \]

\[ \begin{array}{c}
G^+ (+k + \frac{2}{2}) \\
G^- (+k + \frac{2}{2}) \\
G^+ (-k + \frac{2}{2})
\end{array} \]

\[ M_{\times x}(q) \]

Figure 7.2: Connected Feynman diagram structure for the \( \Delta_+ \Delta_\times \) part of \( U_3 \)

is inserted into Mathematica, decomposed, and integrated, the only parts of the \( |\Delta_{\pm}|^2 \) terms that give non-zero G-L parameters are those that contain \( M_{x/y} q_{y/x} \). The values of the constants obtained by integrating the \( M_{x/y} q_{y/x} \) terms are exactly opposite to obtained by integrating the \( M_{x/y} q_{x/y} \) terms, as expected for symmetry. The only non-zero contributions from the ‘cross terms’ (those that contain \( \Delta_\times \)) come from \( M_{x/y} q_{y/x} |\Delta_\times|^2 \), and they are \( \approx 2\% \) of the magnetic terms described above. They thus act as a small correction to the larger terms, and display the expected symmetry properties.

There is no non-zero \( M_z \) portion, at least up to second order. There are also no non-zero \( M q_{x/y} q_{x/y} \) terms. A previous Ginzburg-Landau analysis of a system similar to ours by Michael Achermann predicted the magnetic terms allowable under the system’s
7.2 Computational Work

The $U_2$ terms are relatively straightforward to implement, especially as we’re making the assumption that the derivatives of $M_{x,y,z}$ are negligible - eg. ignoring all magnetic gradient terms. The only parts we have to put into the G-L energy are therefore simple free energy costs to having a non-zero magnetic order parameter.

The $U_3$ terms are a little trickier - our G-L constants end up looking a little different to the ones we’ve obtained so far. Recalling eq. 6.23, a single $q_x/y$ will result in a factor of $-i\partial_x/y$ when applied to $\Delta^*_t/s$, and a factor of $i\partial_x/y$ when applied to $\Delta^*_t/s$. This means that the magnetic part of our updated G-L Free energy for a superconductor occupying the half-space $x > 0$ is

$$F_{Mag} = \int_0^\infty K_{ms} M_y i (\Delta^*_t \partial_x \Delta_s - \Delta_s \partial_x \Delta^*_t) + K_{mt} M_y i (\Delta^*_t \partial_x \Delta_t - \Delta_t \partial_x \Delta^*_t)$$

$$+ K_{mst} M_y i (\Delta^*_t \partial_x \Delta_s - \Delta_s \partial_x \Delta^*_t + \Delta^*_s \partial_x \Delta_t - \Delta_t \partial_x \Delta^*_s) + K_y M_y^2 dx.$$  (7.23)

This is a rather pleasing result, and closely resembles the approximation we obtained in eq. 4.40 with the caveat that $M_y$ is not directly analogous to the $A_y$ discussed in Chapter 4: $M_y$ is a measurement of the magnetization of the system, rather than the vector potential. $F_{Mag}$ can thus be taken as representing a bilinear coupling between the system’s magnetization and the superconducting order parameters. This suggests that what magnetism arises is intrinsic to the superconducting state, requiring spatial inhomogeneity and the breaking of TRS to appear. A similar coupling between magnetization and the superconducting state was obtained by Yang et al. in a centrosymmetric system [67].

Like $\alpha_{ts}$, $K_{ms}$ and $K_{mt}$ are zero for $\lambda = 0$. These terms display the ‘magneto-electric effect’, in which the breaking of inversion symmetry (and therefore the presence of spin-orbit coupling) allows coupling between the system’s magnetization and the flow of a supercurrent described by the $K_{ms}$ and $K_{mt}$ terms [68]. Inversion symmetry breaking is not required for $K_{mst}$ to be non-zero, and as such the $K_{mst}$ term can be understood as symmetries, and his results very much resemble ours [66]. $M_z$ terms were not ruled out by his analysis, but not all permissible terms are necessarily non-zero.

Figure 7.3: Connected Feynman diagram structure for the $\Delta_+ \Delta_-$ part of $U_3$
representing the aforementioned intrinsic magnetization, which is induced by $\Delta_t$ and $\Delta_s$. The presence of both $\Delta_t$ and $\Delta_s$ does imply that this coexisting state violates inversion symmetry even if the system’s normal state does not, however.

Implementing eq. 7.23 in MATLAB allows us to incorporate $M$ into our simulations. The first thing to do is compare the results of our new and improved program with those of the initial pure G-L model in Chapter 4. As Fig. 7.4 shows, they are quite similar. Just as before, a magnetic order parameter appears close to the surface both without and with spin-orbit coupling (see Fig. 7.4 and Fig. 7.5, respectively). The fact that it decays away over the same length as $\Delta_s$ is a consequence of us not enforcing a free energy cost for non-zero magnetic gradients as we did in Chapter 4. While our results may initially seem to indicate that the superconducting material has a non-zero total magnetization, this is because we are only considering one boundary - if we introduce another boundary at $x = 250\xi_t$, then the magnetizations at each surface are opposite (see Fig. 7.6), and so considering Meissner screening as in Chapter 4 will not strongly modify our calculations. But what effect does the appearance of the magnetic order parameter have on the availability of TRSB? It’s difficult to quantify from these plots - as we can see from eq. 7.23, $M$ can only appear when there is a phase difference between the two order parameters. This means that we should be examining the effects of $M$ on $\phi$.

Fig. 7.7 shows the effect of the magnetic term on $\phi$ by plotting the difference between the $\phi$-values obtained with and without the inclusion of $M$. At first it may seem that $M$ suppresses $\phi$, as the magnetically-active system has a lower $\phi$ at the border. On closer inspection however, it has a higher value of $\phi$ around the phase peak and past it. What’s going on? In fact the inclusion of $M$ slightly reduces the free-energy cost to having a non-zero $\phi$ gradient, allowing steeper gradients to arise and resulting in the higher-peak, lower-boundary-value behaviour we have observed. Given that we saw how ‘gradient suppression’ can prevent TRSB from occurring in the previous chapter, we can predict
that the inclusion of $M$ will very slightly increase the TRSB availability of our system.

But what of the centrosymmetric system? The value of $\phi$ is fixed at $\frac{\pi}{2}$, so examining the effect of $M$ on it would be rather pointless. We instead examine the effect of $M$ on $\Delta_s$; Fig. 7.8 shows this by plotting the difference between $|\Delta_s|$ with $M$ and without. The effect is rather straightforward: as in Fig. 4.7, the magnetic order parameter slightly promotes the appearance of $\Delta_s$, although to a significantly lesser degree compared to Fig. 4.7 as the magnetic order parameter is far smaller in this case. As $\lambda = 0$ means $\phi = \frac{\pi}{2}$, any appearance of $\Delta_s$ will constitute TRSB. The magnetic order parameter will thus also increase TRSB availability in our system.

We at last have all the tools to investigate the availability of TRSB in a system with varying border-suppression, so it is finally time to do so.

### 7.2.1 The TRSB Scan Program

Unfortunately, determining the effect of border suppression on TRSB availability is rather difficult; simply creating and examining a lot of individual plots with varying constants could yield some understanding, but carries the risk of missing subtle or niche effects. An obvious “brute force” solution is to construct a series of plots similar to Figs. 5.15 and 5.16 at varying suppression levels, but this is impractical. It would require one minimization per ‘pixel’, and if each minimization took $\sim 30$ seconds (a generously small estimate) a $100 \times 100$ plot would take over 80 hours.

The solution then is to ‘scan’ for TRSB. We know from Chapter 4 where in our parameter-space TRSB occurs in the bulk, so all we need do is create a program that scans down temperature $T$ at a set $V_t/V_s$, looking for a non-zero phase difference. When it finds one, it can increase the $V_t/V_s$ ratio and continue looking. This is the basic concept of what we shall call the ‘TRSB scan program’, though the program itself is rather more complex. A more complete logic map can be found in Appendix B for those interested
The Magnetic Potential

Figure 7.6: $\Delta_t$, $\Delta_s$, $\phi$, and $M_y$ vs $x$ for $N = 2000^2$, $V_s = 0.5$, $V_t = 0.468$, $\mu = 0.3$, $\lambda = 0.09$, $k_B T = 0.0045$, and 90% suppression at both $x = 0$ and $x = 250\xi_t$. $\Delta$ values and $M_y$ are in units of $2t$. Some results have been multiplied or divided by 100 to be visible on the same axes as $\Delta_{t/s}$.

(see Fig. B.1).

The most important addition to this basic premise is that when the program finds TRSB, it generates a small range of G-L variables linearly connecting the two formally-calculated values that the TRSB was found between - a passable approximation given the restricted temperature-scale in question - and then does a ‘fine scan’ to find the edge of the TRSB region with far greater precision than would otherwise be possible in a reasonable amount of time. Despite these extra minimizations in the ‘fine scan’, this program allows us to obtain a good picture of the TRSB area of parameter-space 5-20 hours - much more quickly than the alternative.
7.2 Computational Work

Figure 7.7: The difference between $\phi$ with and without the inclusion of the magnetic order parameter vs $x$ for $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0.09$ and $k_B T = 0.0045$.

Figure 7.8: The difference between $|\Delta_s|$ with and without the inclusion of the magnetic order parameter vs $x$ for $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0$ and $k_B T = 0.0045$. $\Delta$ values are in units of $2t$. At the boundary, this translates to a difference a little under 1%.
7.3 TRSB In the Phase Diagram

Using the TRSB scan program, we are able to gain a picture of the TRSB availability in our system for a wider variety of parameters. Figs. 7.9 and 7.10 show TRSB availability for the system including the effects of the magnetic order parameter for broken inversion symmetry ($\lambda = 0.09$) non-broken inversion symmetry ($\lambda = 0$) respectively, while Fig. 7.11 shows the difference between a system with and without the inclusion of the magnetic order parameter. This latter is only done for the $\lambda = 0$ case, as the difference is found to be negligible for $\lambda = 0.09$.

![Diagram showing TRSB availability for varying surface suppression](image)

Figure 7.9: TRSB scan program results showing TRSB availability vs $k_B T$ and $V_t/V_s$ for varying surface $\Delta_t$ suppression and $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0.09$. $k_B T$ values are in units of $2t$. We find three distinct regions: one with no TRSB at all, one where TRSB occurs in the bulk, and one where TRSB occurs at the surface but not in the bulk.

7.3.1 Analysis

Figures 7.9 and 7.10 show that suppressing $\Delta_t$ allows far greater availability of TRSB in the system, whether we have spin-orbit coupling or not. The inclusion of the magnetic order parameter doesn’t affect this much - for $\lambda = 0$ it very slightly increases the temperature at which TRSB occurs, more so as $V_t/V_s$ increases. This is unsurprising, but bodes very well for Timm et al.’s predictions: their predicted system seems not only to be
### 7.3 TRSB In the Phase Diagram

Figure 7.10: TRSB scan program results showing TRSB availability vs $k_B T$ and $V_t/V_s$ for varying surface $\Delta t$ suppression and $N = 2000^2$, $V_s = 0.5$, $V_t = 0.468$, $\mu = 0.3$, $\lambda = 0$. $k_B T$ values are in units of $2t$. We find three distinct regions: one with no TRSB at all, one where TRSB occurs in the bulk, and one where TRSB occurs at the surface but not in the bulk.

Viable, but far more likely to occur than the bulk-TRSB system that may perhaps have been expected in the case of spin orbit coupling.

The lesser effect on TRSB availability that the magnetization has for $\lambda \neq 0$ systems can be understood by returning to eq. 7.23; the free energy of the magnetization-superconductivity coupling $K_{mst}$ term will be minimized for a phase difference of $\frac{\pi}{2}$, which is the only phase difference possible in the absence of spin-orbit coupling. In non-centrosymmetric systems however, the phase difference will be very small on the edges of the TRSB area, which is where the magnetic order parameter can be a factor in TRSB availability. This means that the gradient-mixing term will be less significant, and thus that the magnetic order parameter will have a lesser effect on the phase behaviour of the system. Conversely, the increase in TRSB availability for full $\Delta t$ suppression is greater in the non-centrosymmetric system. As full $\Delta t$ suppression cannot fail to move the system to full $\Delta s$ dominance at the surface (effectively forcing $V_t/V_s = 0$ at $x = 0$), we may surmise that TRSB is more vulnerable to being ‘suppressed away’ (as it is in Fig. 6.7b) for $\lambda = 0$ than for $\lambda \neq 0$.

Finally, we should note the effect of suppression is not linear - the difference between 50% suppression and 25% suppression is greater than the difference between 75% and 50%,
Figure 7.11: TRSB scan results showing TRSB availability vs $k_B T$ and $V_t/V_s$ for 50% surface $\Delta_t$ suppression and $N = 2000^2, V_s = 0.5, V_t = 0.468, \mu = 0.3, \lambda = 0$. $k_B T$ values are in units of $2t$. The darker blue area on the plot indicates surface TRSB which occurs only when the magnetic order parameter is included in the system.

for example. Thus even a small suppression can make a fairly significant difference in the availability of TRSB, and there is very little practical difference between 70% and 100% suppression for our purposes.

There are many different kinds of triplet pairing however, and we have examined but one. The form of the magnetic contribution to the free energy will be different for different pairings, and thus the effect of $M$ on the TRSB availability may be different. This may be a topic of future study.
Conclusions

In this thesis we have investigated the appearance of a localized TRSB state at the surface of a superconductor where both singlet and triplet Cooper pair superconducting states can occur, both in the presence and the absence of inversion symmetry breaking. In the first chapter, we learned the phenomenology of superconductivity and the basics of the BCS theory. Our work was motivated by the fact that this could not explain all observed forms of superconductivity, and that a team of researchers had made interesting predictions about the behaviour of a superconductor that lacked inversion symmetry. This led to our stated aim of constructing a microscopically-connected phenomenological model of a similar system that we could use to investigate the phenomena they described. To this end, we spent the next chapter arming ourselves with important techniques from the quantum theory of many-particle systems.

In Chapter 3 we made a quick treatment of the Bogoliubov Hamiltonian, and learned that the rapid increase in complexity inherent in extending the mean-field technique made using it for the case we wanted to examine rather impractical. We then introduced the phenomenological Ginzburg-Landau theory, the relative simplicity and flexibility of which made it more appropriate for studying the inhomogeneous systems that we are concerned with. We connected the G-L theory to the microscopic picture to ensure our results would be accurate, which involved using a Linked Cluster Expansion to obtain the bulk G-L constants, the gradient terms, and finally the magnetic contribution to the free energy of our system. This model was shown to agree with the mean-field theory bulk calculations only reasonably close to the critical temperature, so we limited our work to areas near $T_c$.

Having derived a complete G-L free energy from the microscopic case, we finally developed a program to construct the phase diagram as a function of the temperature and the ratio of the interaction potentials for the singlet and triplet pairings, and found that boundary suppression of one of the superconducting order parameters vastly increases the availability of TRSB in our system. The magnetic order parameter appeared near the surface as predicted by others [63], but only fractionally increased the parameter space where TRSB occurred. We are at last in a position to draw some conclusions.

8.1 The Origin of Surface TRSB

Timm et al. predicted that a superconductor lacking inversion symmetry (and thus displaying spin-orbit coupling) would display TRSB at the surface, but not in the bulk. They were motivated to look for TRSB due to the existence of zero-energy surface states in their model; these could be shifted away from zero-energy (thus lowering the free energy) by a surface-TRSB state. Similar arguments have been made by other authors concerning the Cuprates [6]. We have shown here that surface-TRSB states are not only
possible, but occupy far more of our parameter space than bulk TRSB systems (although bulk TRSB systems are possible). We also observed an unexpected ‘phase peak’ in our non-centrosymmetric system.

We’ve shown that the occurrence of this peak is because $\Delta_t$ suppression at the surface can artificially move the system to full singlet dominance, and not due to some error on our part. There is also evidence that it shows up in Timm et al.’s results, which is encouraging. If this ‘phase peak’ occurs in future investigations into surface-TRSB in similar systems, then our work will be substantially vindicated.

Investigations into the origin of the phase peak also led to the development of the ‘local approximation’ for the phase, which as discussed in Chapter 6 revealed that we can view border suppression of $\Delta_t$ as artificially changing the $V_t/V_s$ ratio. The effect of this is to essentially locally move the system to the left on Figs. 5.15 and 5.16. This conception is a new and intuitive way to understand the origin of the surface TRSB state: In our model, the surface-TRSB is enabled by ‘proximity’ in parameter space to the bulk TRSB state.

Our and Timm et al.’s interpretations are complementary: the zero-energy surface states responsible for TRSB in the microscopic theory only appear at surfaces where the triplet state is suppressed due to the symmetry-imposed pair-breaking effect. This is represented in the G-L free energy by the boundary suppression of $\Delta_t$, which we have argued here is responsible for the surface TRSB states. We can thus see that both approaches are entirely physically consistent.

8.2 The Magnetic Order Parameter

Our results indicate that the surface TRSB state is always accompanied by a magnetization, which corroborates the microscopic analysis of Timm et al. [53]. We included the magnetization as a separate order parameter, and found that doing so did not significantly affect the appearance of the surface TRSB state. In a two-sided ‘slab-like’ system, this magnetization had opposite signs on opposite sides of the material, thus likely requiring minimal screening currents. Although we did not explicitly account for the possibility of such currents, the very small values obtained for the magnitude of the magnetization indicate that doing so would not materially change our results.

8.3 The LCE as a Method of Connecting the Microscopic and Macroscopic

Finally, we have shown the merit of using a Linked Cluster Expansion to connect a microscopic Bogoliubov Hamiltonian to a macroscopic, phenomenological theory. The results we obtained with this technique were very much in line with previous predictions, from the phase behaviour of the system to the appearance of the magnetic order parameter. The divergence of $\beta_{s,t}$ as $T$ approaches zero indicates that these results are only quantitatively valid close to the critical temperature $T_c$. Timm et al.’s work predicted a TRSB state at $T \approx 0.1T_c$, which is clearly beyond the limits of quantitative validity for our technique.

Nevertheless, we can expect our results to be qualitatively accurate even at lower temperatures. The core mechanism whereby surface suppression causes TRSB is ‘movement’ though the bulk TRSB regime due to a change in the effective $V_t/V_s$ ratio, and this will remain the same regardless of temperature as long as a bulk TRSB exists somewhere in parameter space as we approach $T = 0$. Nothing in our investigations has given us reason
to suspect that it would not. Thus while it is possible that a different mechanism is at work in Timm *et al.*’s system, we certainly do not require one to explain its behaviour.

### §8.4 Future Study

The success of our microscopically-connected G-L method in analysing the behaviour of a complex system indicates that our techniques could be used to study other cases too complex for pure microscopic treatment. These may include systems close to a ferromagnetic phase transition, interruptions in the crystal structure of the superconductor such as ‘domains’ where there is opposite-sign spin-orbit coupling [69], or the natural progression of considering other non-centrosymmetric systems with different triplet pairings [70].
This appendix contains samples of the MATLAB and Wolfram Mathematica code that was used to obtain the results presented in this thesis. First is the MATLAB function that defines the Ginzberg-Landau free energy that we minimize with `fminunc()`. This is the final version, including all gradient and magnetic terms:

### A.1 MATLAB G-L Free Energy

```matlab
function [ freeEnergy, grad ] = unifiedSuperGLOBAL_MAG(all_guesses)
% Simulates free energy of a more complex superconductor

global XINC;
global ALPHA_T;
global ALPHA_S;
global BETA_T;
global BETA_S;
global GAMMA_1;
global GAMMA_2;
global ALPHA_TS_BASE;
global K_TS;
global K_S;
global ALPHABETA_S;
global ALPHABETA_T;
global BORDER_RATIO;
global BULK_T_RE;
global BULK_T_IM;
global M_GRAD_T;
global M_GRAD_S;
global M_GRAD_MIX;
global M_2;

deltaLength = length(all_guesses)/5;

delta_guesses_t_real = all_guesses(1:deltaLength);
delta_guesses_s_real = all_guesses(deltaLength + 1:2*deltaLength);
delta_guesses_t_im = all_guesses(2*deltaLength + 1:3*deltaLength);
delta_guesses_s_im = all_guesses(3*deltaLength + 1:4*deltaLength);
```

MagPart = all_guesses(4*deltaLength + 1:5*deltaLength);

delta_guesses_t = delta_guesses_t_real + 1i.*delta_guesses_t_im;
delta_guesses_s = delta_guesses_s_real + 1i.*delta_guesses_s_im;

bulk_delta_t = BULK_T_RE + 1i.*BULK_T_IM;

derMat = diag(ones(1,deltaLength)) - diag(ones(1,deltaLength - 1),1);
derMat(deltaLength,deltaLength) = 0;
gradDerMat = derMat - diag(ones(1,deltaLength - 1),-1) +
diag(ones(1,deltaLength));
gradDerMat(1,1) = 1;
gradDerMat(deltaLength,deltaLength) = 1;
magDer = diag(ones(1,deltaLength - 1),1) - diag(ones(1,deltaLength - 
1),-1);
alpha_t = ALPHA_T;
beta_t = BETA_T;
alpha_s = ALPHA_S;
beta_s = BETA_S;
gamma_1 = GAMMA_1;
gamma_2 = GAMMA_2;
alpha_coupling = ALPHA_TS_BASE;
K_ts = K_TS;
border_suppress = BORDER_RATIO.^2;
charLength_noAlpha_t = 1;
charLength_noAlpha_s = K_S;
boundPicker = zeros(deltaLength,1);
alphabeta_s = ALPHABETA_S;
alphabeta_t = ALPHABETA_T;
boundPicker(1,1) = 1;

gradM_t = M_GRAD_T; gradM_s = M_GRAD_S; gradM_mix = M_GRAD_MIX;

freeEnergy = ... t-state energy: 1e15*( abs(delta_guesses_t(1)).^2 -
border_suppress.*abs(bulk_delta_t).^2 ).^2 ...
+ alpha_t.*sum(abs(delta_guesses_t).^2) + beta_t.*sum(abs(delta_guesses_t).^4)
... + ((charLength_noAlpha_t/XINC).^2)*sum(abs((derMat*delta_guesses_t).^2) ... 
... s-state energy:
+ alpha_s.*sum(abs(delta_guesses_s).^2) + beta_s.*sum(abs(delta_guesses_s).^4)
... + ((charLength_noAlpha_s/XINC).^2)*sum(abs((derMat*delta_guesses_s).^2) ... 
... interaction energy:
+ gamma_1*sum((abs(delta_guesses_t).^2).*abs(delta_guesses_s).^2)) ...
+ ((K_ts/XINC).^2)*sum((derMat*delta_guesses_t).*(derMat*conj(delta_guesses_s))
+ ... 
(denMat*delta_guesses_s).*(derMat*conj(delta_guesses_t)) ...
+ gamma_2*( sum( (delta_guesses_t.^2).*abs(denst_guesses_t).^2 ) )... 
+ sum( (conj(denst_guesses_t).^2).*abs(denst_guesses_t).^2 )... 
+ sum((alpha_coupling + 2.*alphabeta_s.*abs(denst_guesses_s).^2)... 
+ 2.*alphabeta_t.*abs(denst_guesses_t).^2).*(
(denst_guesses_t.*conj(denst_guesses_s)))... 
+ (conj(denst_guesses_t).*denst_guesses_s) )) ... 
... magnetic energy: 
+ sum(MagPart.*( -2.*(gradM_s./XINC).*imag( 
derMat*conj(denst_guesses_s).*conj(denst_guesses_s) ) ... 
- 2.*(gradM_t./XINC).*imag( derMat*denst_guesses_t).*conj(denst_guesses_t) )... 
- 2.*(gradM_mix./XINC).*imag(( derMat*denst_guesses_s).*conj(denst_guesses_t) 
+ (derMat*denst_guesses_t).*conj(denst_guesses_s) ) )))... 
+ M_2.*sum(MagPart.^2); 

if nargout > 1 ¾ this is the gradient of our function with respect to 
each element of all guesses 
grad = ... t-state (real part): 
[(4e15).*denst_guesses_t_real(1).*abs(denst_guesses_t(1)).^2 ... 
- border_suppress.*abs(bulk_denst_t).^2 ).*boundPicker ... 
+ 2.*alpha_t.*denst_guesses_t_real ... 
+ 4.*beta_t.*(denst_guesses_t_real.^2 + 
denst_guesses_t_real.*(denst_guesses_t_imag.^2))... 
+ 2.*((charLength_noAlpha_t/XINC).^2).*gradDerMat*denst_guesses_t_real)...
+ 2.*gamma_1.*(denst_guesses_t_real.*abs(denst_guesses_s).^2)... 
+ 4.*gamma_2.*(denst_guesses_t_real.*(denst_guesses_s_real.^2 ... 
+ delta_guesses_s_imag.^2) ... 
+ 2.*delta_guesses_t_imag.*delta_guesses_s_real.*delta_guesses_s_imag) ... 
+ 2.*alpha_coupling.*delta_guesses_s_real ... 
+ 2.*alphabeta_s.*denst_guesses_s_real.*abs(denst_guesses_s).^2 ... 
+ 2.*alphabeta_t.*( 6.*denst_guesses_s_real.*(denst_guesses_t_real.^2 ... 
+ 4.*denst_guesses_t_real.*denst_guesses_t_imag.*denst_guesses_s_imag ... 
+ 2.*(K_ts/XINC).^2).*gradDerMat*denst_guesses_s_real) ... 
+ 2.*MagPart.*(gradM_t./XINC).*magDer*denst_guesses_t_imag)...
- 2.*MagPart.*(gradM_mix./XINC).*magDer*denst_guesses_s_imag); ... 
... s-state (real part): 
2.*alpha_s.*denst_guesses_s_real ...
+ 4.*beta_s.*(denst_guesses_s_real.^2 + 
denst_guesses_s_real.*(denst_guesses_s_imag.^2))... 
+ 2.*((charLength_noAlpha_s/XINC).^2).*gradDerMat*denst_guesses_s_real)...
+ 2.*gamma_1.*(denst_guesses_s_real.*abs(denst_guesses_t).^2)... 
+ 4.*gamma_2.*(denst_guesses_s_real.*(denst_guesses_t_real.^2 ... 
- delta_guesses_t_imag.^2) ... 
+ 2.*delta_guesses_t_imag.*denst_guesses_t_real.*delta_guesses_s_imag) ... 
+ 2.*alpha_coupling.*denst_guesses_t_real ... 
+ 2.*alphabeta_t.*denst_guesses_t_real.*abs(denst_guesses_t).^2 ... 
+ 2.*alphabeta_s.*( 6.*denst_guesses_t_real.*(denst_guesses_s_real.^2 ... 
+ delta_guesses_t_imag.^2) ...
\begin{align*}
+ 4.\delta_{\text{guesses\_s\_real}} \cdot \delta_{\text{guesses\_s\_im}} \cdot \delta_{\text{guesses\_t\_im}} \\
+ 2.\delta_{\text{guesses\_s\_im}} \cdot \delta_{\text{guesses\_t\_real}} \\
+ 2.\delta_{\text{guesses\_t\_im}} \cdot \delta_{\text{guesses\_t\_real}} \\
+ 2.\text{(charLength\_noAlpha\_t/XINC)}^2 \cdot \text{(gradDerMat} \delta_{\text{guesses\_t\_real}} \\
+ 2.\text{MagPart} \cdot \text{gradM\_s} \cdot \text{XINC} \cdot \text{(magDer} \delta_{\text{guesses\_s\_im}} \\
- 2.\text{MagPart} \cdot \text{gradM\_mix} \cdot \text{XINC} \cdot \text{(magDer} \delta_{\text{guesses\_t\_im}} \\
\cdot \text{t\_state (imaginary part):} \\
(4e15) \cdot \delta_{\text{guesses\_t\_im}} \cdot \text{(abs(} \delta_{\text{guesses\_t\_im}} \cdot \text{)^2} \\
- \text{border\_suppress} \cdot \text{abs(bulk\_delta\_t} \cdot \text{)^2} \cdot \text{boundPicker} \\
+ 2.\alpha_t \cdot \delta_{\text{guesses\_t\_im}} \\
+ 4.\beta_t \cdot \text{(delta\_guesses\_t\_im} \cdot \text{^3} \\
+ \delta_{\text{guesses\_t\_im}} \cdot \text{(delta\_guesses\_t\_real} \cdot \text{^2}) \\
+ 2.\text{(charLength\_noAlpha\_t/XINC)}^2 \cdot \text{(gradDerMat} \delta_{\text{guesses\_t\_im}} \\
+ 2.\gamma_{\text{t}} \cdot \text{(delta\_guesses\_t\_im} \cdot \text{(abs(} \delta_{\text{guesses\_t\_im}} \cdot \text{)^2} \\
+ 2.\text{alpha\_coupling} \cdot \delta_{\text{guesses\_t\_im}} \\
+ 2.\alpha_{\text{t}} \cdot \delta_{\text{guesses\_t\_im}} \\
+ 4.\beta_{\text{t}} \cdot \text{(delta\_guesses\_t\_im} \cdot \text{^3} \\
+ \delta_{\text{guesses\_t\_im}} \cdot \text{(delta\_guesses\_t\_real} \cdot \text{^2}) \\
- 2.\text{(charLength\_noAlpha\_s/XINC)}^2 \cdot \text{(gradDerMat} \delta_{\text{guesses\_s\_im}} \\
+ 2.\gamma_{\text{s}} \cdot \text{(delta\_guesses\_s\_im} \cdot \text{(abs(} \delta_{\text{guesses\_s\_im}} \cdot \text{)^2} \\
+ 2.\text{alpha\_coupling} \cdot \delta_{\text{guesses\_s\_im}} \\
+ 2.\alpha_{\text{s}} \cdot \delta_{\text{guesses\_s\_im}} \\
+ 4.\beta_{\text{s}} \cdot \text{(delta\_guesses\_s\_im} \cdot \text{^3} \\
+ \delta_{\text{guesses\_s\_im}} \cdot \text{(delta\_guesses\_s\_real} \cdot \text{^2}) \\
- 2.\text{gradM\_s} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_s}\cdot \text{conj(delta\_guesses\_s}) \\
- 2.\text{gradM\_t} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_t}\cdot \text{conj(delta\_guesses\_t}) \\
- 2.\text{gradM\_mix} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_t}\cdot \text{conj(delta\_guesses\_t}) \\
\cdot \text{magnetic\_order\_parameter:} \\
- 2.\text{gradM\_s} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_s}\cdot \text{conj(delta\_guesses\_s}) \\
- 2.\text{gradM\_t} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_t}\cdot \text{conj(delta\_guesses\_t}) \\
- 2.\text{gradM\_mix} \cdot \text{XINC} \cdot \text{(imag(} \text{derMat} \cdot \text{(delta\_guesses\_t}\cdot \text{conj(delta\_guesses\_t}) \\
\end{align*}
A.2 Mathematica $q$-decomposition example

Next is an example of the $q$-decompositions that we conduct in Mathematica. The following is for the $|\Delta_s|^2$ part of the $|\Delta_u|^2$ term.

ReplaceAll\[ 1/2 ( 1 - 2 Re[V Conjugate[U]] ),
{V \rightarrow 1/Sqrt[2]*( Sin[ky a] + qy a/2 Cos[ky a] + i Sin[kx a] + i qx a/2
Cos[kx a])/ Sqrt[(Sin[ky a] + qy a/2 Cos[ky a])^2 + (Sin[kx a] + qx a/2
Cos[kx a])^2],
U \rightarrow 1/Sqrt[2]*(-Sin[ky a] + qy a/2 Cos[ky a] - i Sin[kx a] + i qx a/2
Cos[kx a])/ Sqrt[(-Sin[ky a] + qy a/2 Cos[ky a])^2 + (-Sin[kx a] + qx a/2
Cos[kx a])^2])

FullSimplify[ComplexExpand[Assumptions \rightarrow \{Element[a, Reals], Element[kk,  
Reals], Element[ky, Reals], Element[qy, Reals], Element[qx, Reals]\}]

deltasexpanded = Series[%, \{qx, 0, 2\}, \{qy, 0, 2\}]

deltasexpanded2 = FullSimplify[ComplexExpand[deltasexpanded],
Assumptions \rightarrow \{Element[a, Reals], Element[kk, Reals], Element[ky, Reals],  
Element[qy, Reals], Element[qx, Reals]\}]

deltasorder2q = deltasexpanded2;
deltassimpoqPM = FullSimplify[deltasorder2q /. \{qx \rightarrow 0, qy \rightarrow 0\}]
deltassimp2qPM = FullSimplify[Coefficient[deltasorder2q, qx^2] /. \{qx \rightarrow 0, qy \rightarrow 0\}]
deltassimp2qyPM = FullSimplify[Coefficient[deltasorder2q, qy^2] /. \{qx \rightarrow 0, qy \rightarrow 0\}]

G[\epsilon_-, \omega_-] := 1/(\omega - \epsilon);

epsilononorder2q = Series[ (1/\beta)*Sum[ G[\epsilon a, \omega]*G[\epsilon b, -\omega]/,. 
{\omega \rightarrow I*(2 n + 1)*\pi/\beta}, \{n, -Infinity, Infinity\} ]/. 
{\epsilon a \rightarrow \epsilon [kx + qx/2, ky + qy/2], \epsilon b \rightarrow \epsilon[kx - qx/2, ky - qy/2]}, 
{qx, 0, 2}, \{qy, 0, 2\} ];
Code Samples

\[ \text{epsilonsimpnoqPLUS} = \text{FullSimplify}[\epsilon_{\text{order2q}} / . \{\text{qx} \rightarrow 0, \text{qy} \rightarrow 0\}] \]
\[ \text{epsilonsimp2qxPLUS} = \text{FullSimplify}[\text{Coefficient}[\epsilon_{\text{order2q}}, \text{qx}^2] / . \{\text{qx} \rightarrow 0, \text{qy} \rightarrow 0\}] \]
\[ \text{epsilonsimp2qyPLUS} = \text{FullSimplify}[\text{Coefficient}[\epsilon_{\text{order2q}}, \text{qy}^2] / . \{\text{qx} \rightarrow 0, \text{qy} \rightarrow 0\}] \]

\[ \text{epsilonsimpnoqPLUS} = \{\text{epsilonsimpnoqPLUS}\} / . \{\epsilon[kx, ky] \rightarrow \epsilon\} \]

\[ \text{epsilonsimp2qyPLUS} = \text{epsilonsimp2qyPLUS} / . \{\text{Derivative}[0, 2][\epsilon][kx, ky] \rightarrow a^2*(2*t*\cos[a*ky] + \alpha*(((-3 + \cos[2*a*kx])*\sin[a*ky]^2)/ (2*(\sin[a*kx]^2 + \sin[a*ky]^2)^2) - (3/2))) + \alpha*(\cos[a*ky]^2/Sqrt[\sin[a*kx]^2 + \sin[a*ky]^2]), \text{Derivative}[0, 1][\epsilon][kx, ky] \rightarrow 2*a*t*\sin[a*ky] + \alpha*((a*\cos[a*ky]*\sin[a*ky])/Sqrt[\sin[a*kx]^2 + \sin[a*ky]^2]), \epsilon[kx, ky] \rightarrow \epsilon\} \]

\[ \text{fullepsilonPLUS} = \{\text{epsilonsimpnoqPLUS} + \text{epsilonsimp2qxPLUS}\*\text{qx}^2 + \text{epsilonsimp2qyPLUS}\*\text{qy}^2\} / . \{\epsilon[kx, ky] \rightarrow \epsilon\} \]

\[ \text{DeltaSplusTerm} = (\text{epsilonsimpnoqPLUS}\*\text{fulldeltasPM} + \text{deltasimpnoqPM}\* (\text{epsilonsimp2qxPLUS}\*\text{qx}^2 + \text{epsilonsimp2qyPLUS}\*\text{qy}^2)) / . \{\epsilon \rightarrow -0.3 - 2 t \cos[ky \ a] - 2 t \cos[kx \ a] + \alpha*Sqrt[\sin[ky \ a]^2 + \sin[kx \ a]^2]\}; \]
\[ \text{DeltaSplusTerm} = \text{DeltaSplusTerm} / . \{t \rightarrow \text{TVAL}, \beta \rightarrow \text{BETA}, a \rightarrow 1, \alpha \rightarrow \text{ALPHA}\} \]

\[ \text{plusSqx} = \text{NIIntegrate}[1/(4 \pi^2)* \text{Coefficient}[\text{DeltaSplusTerm}, \text{qx}^2], \{\text{ky}, -\pi, \pi\}, \{\text{kk}, -\pi, \pi\}, \text{Method} \rightarrow \text{"LocalAdaptive"}] \]
\[ \text{plusSqy} = \text{NIIntegrate}[1/(4 \pi^2)* \text{Coefficient}[\text{DeltaSplusTerm}, \text{qy}^2], \{\text{ky}, -\pi, \pi\}, \{\text{kk}, -\pi, \pi\}, \text{Method} \rightarrow \text{"LocalAdaptive"}] \]
\[ \text{plusSnoq} = \text{NIIntegrate}[1/(4 \pi^2)*\text{DeltaSplusTerm} / . \{\text{qx} \rightarrow 0, \text{qy} \rightarrow 0\}, \{\text{ky}, -\pi, \pi\}, \{\text{kk}, -\pi, \pi\}] \]
Appendix B

The TRSB Scan Program Logic Map

Figure B.1: Logic map of the TRSB scan program.
Appendix C

Optimising the Programs

C.1 MATLAB

The primary factor that contributes to the time it takes to minimize the G-L free energy is the number of variables it is minimized with respect to. Thus, the most pertinent feature of any system from the perspective of optimization is the number $N$ of $x$-values we evaluate the order parameters over. The final form of the G-L free energy deals with two superconducting order parameters and a magnetic order parameter. The superconducting order parameters are complex, while the magnetic order parameter is assumed to be real. As \texttt{fminunc()} cannot deal natively with complex numbers, we must split each order parameter into its real and imaginary parts. This means that we must minimize the free energy with regard to five variables per $x$-point, which rapidly scales the computational costs associated with doing so. Fig. C.1 shows a log-log plot of the $x$-points vs time, and we can see that the time in seconds taken depends roughly cubically on the $x$-points.

Some readers may note that we are only interested in the phase difference between the order parameters, and that this fact could be leveraged to allow us to only minimize with respect to four variables: $|\Delta_1|, |\Delta_s|, \phi$, and $M_y$. This is true, but unhelpful. MATLAB is aggressively optimised for matrix operations, and in the five-variables system described above all processes necessary to determine the free energy are matrix-based. Expressing the free energy explicitly in terms of $\phi$ introduces exponentials and trigonometric functions, which render the minimization slower than the pure-matrix state despite only requiring $4/5^{th}$ as many variables.

The settings used for the \texttt{fminunc()} command can also have an impact on the time taken to minimize the G-L free energy. We have been utilizing the trust-region algorithm rather than the default quasi-newton algorithm. The trust-region algorithm is significantly faster but requires an objective gradient for each variable to be provided. This introduces more difficulty at the programming stage, but the rewards in performance are well worth it.
Figure C.1: A log-log plot of the $x$-points evaluated vs the time taken to minimize, for a G-L free energy that includes $M_y$.

### C.2 Mathematica

Most of the optimization in Mathematica consisted of trying to get the programs working at all. If `FullSimplify` - which is used several times in the decomposition process - was called on an expression that was too large or complicated, Mathematica froze. This led to the separation of our expressions into $\Delta$, $M$, and $G$-parts, which were each individually decomposed and simplified in Mathematica and before combined and the whole expression being numerically evaluated.

In addition some terms took a long time to process when integrated with the default `Method` setting of `NIntegrate`. These were evaluated with the `LocalAdaptive`, which gave similar results far more quickly. Still others (some $M_z$-parts of the ‘cross-terms’) would not integrate at all with local or global adaptive methods (Mathematica, after some time, simply returned the input), but when evaluated by other methods such as `GaussBerntsenEspelidRule` they were revealed to sum to zero.
Bibliography


