SUPERCONDUCTING ELECTRODYNAMICS OF UNDERDOPED YTTRIUM BARIUM CUPRATE

by

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Abstract

The cuprate high-temperature (high-$T_c$) superconductors remain an important open problem in physics, with currently no microscopic theory that allows calculation of their doping-temperature phase diagram from first principles. The difficulty stems from the importance of electronic correlations, which means that interactions between charge carriers cannot be treated in an average way. However, a good phenomenological understanding of the phase diagram has been developed, with the two most prominent phases being the antiferromagnetic Mott insulating state (AFM) of the undoped parent compound, and the $d$-wave high-$T_c$ superconducting state.

Microwave spectroscopy has been used to study the physics of YBa$_2$Cu$_3$O$_{6+x}$ in a range of dopings near the boundary between the AFM and the superconducting state. A special technique for continuously tuning hole doping in underdoped YBa$_2$Cu$_3$O$_{6+x}$ was developed. This takes advantage of the connection between CuO$_2$-plane doping and the oxygen coordination number of chain Cu atoms. The experiments were performed on a high-quality YBa$_2$Cu$_3$O$_{6.333}$ single crystal, prepared by the U.B.C. superconductivity group, in which cation disorder is estimated to be at the $10^{-5}$ to $10^{-4}$ level.

Microwave spectroscopy was performed using cavity perturbation of a dielectric resonator at 2.64 GHz, at temperatures ranging from 1 K to 150 K. Measurements of surface impedance were made at approximately 40 dopings for in-plane orientation and 13 dopings for $c$-axis orientation. Measurements have been used to obtain the doping dependant microwave conductivity and superfluid density. A model was developed to allow an accurate determination of intrinsic $c$-axis surface impedance in a finite-size spherical sample.

The electrodynamic data have been used in a number of separate analyses, including: placing limits on the magnitude of various electronic orders that might be competing with pure $d$-wave superconductivity; a two-fluid analysis of the microwave conductivity to deter-
mine the quasiparticle relaxation rate; a scaling analysis of the doping-dependent superfluid density in the vicinity of the $T_c \to 0$ quantum critical point; a fluctuation analysis of the normal state paraconductivity; and a determination of the doping dependence of the $d$-wave gap magnitude, nodal gap slope, and charge-current renormalization factor of the $d$-wave quasiparticles.
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Preface

This thesis describes a set of electrodynamic measurements carried out in the Broun lab at Simon Fraser University. The goal of this work was to study the electrodynamics of YBa$_2$Cu$_3$O$_{6+x}$ near the boundary of the superconducting dome. A number of the sections presented here have been adapted from published articles. These include: Chapter 5 from *Apparatus for high resolution microwave spectroscopy in strong magnetic fields* [1]; Section 7.3 and Appendix C from *Stability of nodal quasiparticles in underdoped YBa$_2$Cu$_3$O$_{6+x}$ probed by penetration depth and microwave spectroscopy* [2]; Section 8.1 from *Superfluid density in a highly underdoped YBa$_2$Cu$_3$O$_{6+x}$ superconductor* [3]; and Appendix A from *Effective magnetic penetration depth in superconducting cylinders and spheres with highly anisotropic electrodynamics* [4].

As this is a thesis on experimental results I must inform the reader of a number of conventions in the field. First off, the transition temperatures $T_c$'s of the sample at different dopings are defined as the temperature at which the superfluid density goes to zero for each doping. Due to a lack of an independent, direct method of determining doping $p$, the $T_c$ is used as a proxy. For instance, I will often refer to “the doping at which $T_c =...$”. Further, I will refer to the inverse penetration depth squared $1/\lambda^2$ as the superfluid density $\rho_s$, even though, strictly speaking, $\rho_s = 1/e^2\mu_0\lambda^2$. In the field these two terms, along with the term ‘phase stiffness’, are used interchangeably and they are often normalized to their zero temperature values in plots, to emphasize the important qualitative features.

The introductory chapters provide the context for the experiments. Chapter 1 describes the cuprate phase diagram brought about by the strong electronic correlations present in the cuprate superconductors. The theory of superconductivity is discussed in Chapter 2, starting with London theory, a discussion of the the two-fluid model and finally BCS theory. Chapter 3 shows that the superconductivity in the cuprates is $d$-wave in nature and
discusses the ramifications of this pairing state with regards to the measurements presented in this thesis. Finally, Chapter 4 introduces the effects of fluctuations, both on the superfluid density and the normal-state conductivity.

Following the introduction the main experimental techniques are described: microwave spectroscopy by cavity perturbation in Chapter 5; and the chemistry and doping mechanism of YBa$_2$Cu$_3$O$_{6+x}$, in particular YBa$_2$Cu$_3$O$_{6.333}$ in Chapter 6. The novel method that we developed for varying the doping of a single sample without changing the chemical composition was key to enabling the work presented here.

The emphasis is then on presenting the data, starting with in-plane quantities (surface impedance, superfluid density, and microwave conductivity) in the beginning of Chapter 7. The in-plane data, on their own, can be used in several analyses, and this is carried out next: in Section 7.3 limits are placed on the magnitude of various electronic orders that may be competing with pure $d$-wave superconductivity; a two-fluid analysis of the microwave conductivity to determine the quasiparticle relaxation rate is discussed in Section 7.4; and in Chapter 8 a scaling analysis of the doping-dependent superfluid density in the vicinity of the $T_c \to 0$ quantum critical point is performed, as well as a fluctuation analysis of the normal state paraconductivity.

The $c$-axis data are then presented in Chapter 9. When combined with in-plane data, two new analyses, presented in Chapter 10, become possible: the use of the temperature dependence of the superfluid density to infer properties of the nodal quasiparticles, namely the gap slope near the $d$-wave node, and the extent to which interaction effects renormalize the charge-current carried by the quasiparticles; and two independent estimates of the magnitude of the $d$-wave superconducting gap.

The thesis ends with three appendices: Appendix A on the effective penetration depth in an electrically anisotropic sphere, a necessary ingredient to analysing the $c$-axis data; Appendix B on the effects of sample misalignment with respect to the microwave magnetic fields; and Appendix C on the superfluid density in mixed-symmetry superconducting states.

I would like to thank a number of people who have made this work possible. Special thanks go to my supervisor David Broun who took me on as his first graduate student and taught me the joys of experimental physics. Who knew it was so much like farming? I would like to thank the U.B.C. superconductivity group, in particular Ruixing Liang, Doug
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Chapter 1

Correlated electrons

Within science there are few experimental observations that continue to defy explanation for decades after their discovery. In condensed matter physics, superconductivity has performed this feat twice. After the initial discovery of superconductivity in 1911 by Onnes [5], it took until 1957 for Bardeen, Cooper and Shrieffer [6] to provide a successful microscopic explanation (BCS theory), which qualitatively and quantitatively described the effect. Again, in 1986, a new form of superconductivity, at temperatures never thought possible, was discovered by Bednorz and Müller [7] and theorists were baffled again. The existing BCS theory could not explain superconductivity at temperatures above $\sim 30$ K, but these new materials, the copper oxide high-temperature superconductors, had transition temperatures, $T_c$’s, as high as 160 K. To this day, almost 25 years later, we still have no universally agreed upon theory that predicts superconductivity in these materials at these high temperatures.

It is not only the superconductivity of the cuprates that is baffling, but a number of other features of their doping-temperature phase diagram. With slight chemical modifications many of the cuprates display an antiferromagnetic Mott insulating state, charge ordering, $d$-wave superconductivity, and a wide variety of anomalous electronic properties. Throughout all this is a strong susceptibility to the effects of defects and small changes in chemical composition and structure. This makes understanding their intrinsic properties a formidable challenge and makes it extremely important to perform careful experiments on high quality samples. To this end we have performed high-resolution measurements of the penetration depth, quasiparticle conductivity and resistivity in one of the purest and most perfectly
CHAPTER 1. CORRELATED ELECTRONS

Figure 1.1: Phase diagram of the hole-doped cuprates. At low dopings the cuprates are antiferromagnetic Mott insulators. As doping is increased the antiferromagnetism gives way and a dome of superconductivity appears. The underdoped region is characterized by a large normal state energy gap, dubbed the “pseudogap”, while in the overdoped region the normal state is Fermi-liquid-like.

Ekstrom et al., 2022. The cuprate phase diagram

The physics of the cuprate high temperature superconductors is that of strong Coulomb repulsion in nearly half-filled CuO$_2$ planes [9, 10]. These strong electronic correlations drive diverse phenomena across a much studied, but not fully understood, phase diagram. In most of the cuprates, the carrier concentration can be tuned chemically, a process known as ‘doping’. While both holes and electrons can be doped into various different cuprate materials, in this thesis the hole-doped cuprates are the focus. Thus a hole-doped doping-temperature phase diagram is shown in Figure 1.1. As charge carriers are doped into these materials, the two most prominent electronic states are the antiferromagnetic (AFM) Mott
insulator and the $d$-wave superconductor. At zero doping the cuprates are antiferromagnetic Mott insulators. Increasing the hole doping away from zero rapidly suppresses magnetism and at roughly a doping of $p = 0.05$ superconductivity emerges at low temperatures. In many of the cuprates there is a finite doping range between the antiferromagnetic phase and the superconducting dome and in this region there is often itinerant magnetism at low temperatures [11–13]. However, in YBa$_2$Cu$_3$O$_{6+x}$, the system of interest in this thesis, the two phases nearly meet at zero temperature [14]. Continuing to increase doping increases the superconducting transition temperature until it peaks around $p = 0.19$. Further increases in doping lower $T_c$ until superconductivity disappears around $p = 0.25$. The region to the right of optimal doping is referred to as ‘overdoped’, while the region to the left is referred to as ‘underdoped’.

While the AFM Mott insulating and the optimal-to-overdoped superconducting phases appear to be well understood, the physics of the underdoped part of the phase diagram that lies between them remains firmly incompatible with standard theory. The most prominent feature of this region is a pseudogap that suppresses low energy spin and charge fluctuations and persists above the superconducting transition to a temperature $T^*$ [15–17]. Identifying the nature of the pseudogap state remains a difficult and open problem.

1.1.1 Mott insulator

The common aspect of all cuprate materials is CuO$_2$ planes, into which charge carriers can be doped, and it is in these planes where most of the ‘action’ occurs. In the parent compounds of the high-temperature superconductors the electronic orbitals in the planes are half filled, with one electron (or one hole) per copper atom. From band theory one would expect this to produce a metallic material [18, 19]. However, instead of showing metallic behaviour at half-filling, these materials exhibit insulating behaviour. Materials like this, whose conductivity vanishes as temperature goes to zero, even though band structure predicts metallic behaviour, are known as ‘Mott insulators’, and they are fundamentally different from band insulators. In a band insulator electron motion is blocked by the Pauli exclusion principle: the highest occupied band contains two electrons per unit cell and thus is full. In a Mott insulator, charge conduction is instead blocked by electron–electron repulsion. In a half-filled band, movement of electrons requires the creation of doubly occupied
CHAPTER 1. CORRELATED ELECTRONS

sites. If electron–electron repulsion is strong enough this motion is blocked and the materials are insulating. The only thing that can fluctuate is the spin on each site. Doping, either of holes or electrons, into the plane restores electrical conductivity by creating sites to which the electrons can jump without incurring an additional cost in Coulomb repulsion energy.

While actual charge motion is blocked, virtual fluctuations in a Mott insulator generate a ‘super-exchange’ \cite{20} interaction. Due to the Pauli exclusion principle, double occupancy, even virtual double occupancy, can only occur if the electrons on the doubly occupied site have spins that are antiparallel. Thus a long-range antiferromagnetic order can lower the energy of the system by allowing this virtual double occupancy to occur. In most of the half-filled cuprates, antiferromagnetism sets in at a Néel temperature between 250 and 400 K.

1.1.2 Underdoped

The most prominent feature of the underdoped region is a pseudogap that persists above the superconducting transition temperature to a temperature $T^*$ and suppresses low-energy spin and charge fluctuations \cite{15–17}. The pseudogap is seen most clearly in angle-resolved photo-emission spectroscopy (ARPES) \cite{21–24}. Below the superconducting transition temperature ARPES measurements show a spectrum with a narrow peak, typical of a conventional metal, and the leading edge of the spectrum is set back from the Fermi level, indicating the presence of a gap. Above $T_c$ the quasiparticle peak disappears, but the gap does not, indicating that the quasiparticle peak exists due to the coherence of the superconducting state. Above $T^*$ the gap either closes or its effects are washed out and we regain the ‘normal’ state of the underdoped cuprates. Here there is a large two-dimensional Fermi surface that appears consistent with conventional band theory, while below $T^*$ the gap breaks the Fermi surface up into four hole-like ‘Fermi arcs’ centred on the Brillouin zone diagonals. Quantum oscillation and magnetotransport measurements on the other hand suggest the existence of electron pockets in this doping region \cite{25, 26}. The picture that is currently emerging is that magnetic fluctuations reduce the Brillouin zone and breaking up the large hole-like Fermi surface into a series of electron and hole pockets, with the hole pockets centred on the original Brillouin zone’s diagonals \cite{27}. Interpretations of recent scanning
Figure 1.2: (a) Representation of ARPES spectra for underdoped high-$T_c$ superconductor at momentum near the antinodal point $(0, \pi)$.\(^1\) The narrow peak present below $T_c$ disappears above $T_c$ but the gap remains. (b) ARPES measurements on underdoped cuprates show four ‘Fermi arcs’ centred on the Brillouin zone diagonals.\(^2\) The data were taken on a sample with a doping $p \equiv x = 0.12$. (c) ARPES measurements on overdoped cuprates above $T_c$ and on underdoped cuprates above $T^*$ show a large hole-like Fermi surface.\(^3\)

tunnelling spectroscopy measurements of quasiparticle interference suggest that the ‘Fermi arcs’ terminate on the magnetic Brillouin zone boundary, lending credence to the idea that the magnetic fluctuations are indeed reorganizing the large Fermi surface [28].

The region above $T_c$ has a number of other strange properties. Measurements of the Nernst effect — the transverse voltage induced by a thermal gradient in an applied magnetic field — reveal a larger signal than expected, leading to speculation that there are vortices present in the pseudogap state. The thermal diffusion of these vortices induces a phase-slip voltage that may explain the enhanced Nernst signal [31, 32]. Also, high-field magnetometry reveals excess diamagnetism in this region [33] and both scanning tunnelling microscopy [34] and muon spin resonance [35] detect what appear to be droplets of precursor superconductor. These measurements lend credence to the idea that the pseudogap

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region is characterized by phase-incoherent superconductivity. This idea holds that $T^*(p)$ marks the formation of tightly bound Cooper pairs with long range phase coherence setting in at $T_c(p)$.

Another theory of the pseudogap postulates that $T^*(p)$ marks the boundary of a distinct thermodynamic phase that is competing with superconductivity, must be accompanied by a broken symmetry, and goes to zero at a quantum critical point within the superconducting phase. This idea was initially motivated by the observation near optimal doping of so-called marginal Fermi-liquid behaviour [36], in which unusual power laws in resistivity, optical conductivity and other physical quantities could be understood in terms of scattering from a scale-invariant fluctuation spectrum, as would be expected near a zero-temperature critical point [37]. On crossing $T^*$, these fluctuations should generically condense to form the broken symmetry state of the pseudogap phase. This scenario is seen in the heavy Fermion superconductors, in which superconductivity appears around a magnetic quantum critical point [38], and may apply in the electron-doped materials, where there is evidence of a antiferromagnetic quantum critical point [39]. In the hole-doped materials, however, the situation is much less clear, though recent experiments suggest there is a break in rotational symmetry at $T^*(p)$ [40]. Identifying which, if any, competing order appears at $T^*(p)$ would have strong implications not just for the pseudogap but for the origin of the non-Fermi-liquid behaviour elsewhere in the cuprate phase diagram.

1.1.3 Overdoped

Considering the complexity and lack of consensus that exists concerning the underdoped region of the phase diagram, the overdoped region is remarkably simple. For dopings above the maximum doping for superconductivity the resistivity approaches the $T^2$ temperature dependence expected of a Fermi liquid [41], and even well below the maximum doping for superconductivity angle-resolved photo-emission spectroscopy (ARPES) reveals the predicted large hole-like Fermi surface [30]. Recent quantum oscillation measurements confirm the Fermi liquid nature of the normal state, showing an oscillation frequency that corresponds well to the ARPES Fermi surface, and a temperature dependence that agrees with the predictions of Fermi liquid theory [42, 43]. Also noteworthy is that the thermal transition into the superconducting state appears to agree well with weak-coupling BCS
theory, with a gap that opens at $T_c$ and, at zero temperature, scales to $T_c$ according to $\Delta(0) \propto k_B T_c$. The large Fermi surface appears to survive down to optimal doping, while the resistivity smoothly evolves from a quadratic to a linear temperature dependence.

The pseudogap state smoothly evolves between two well understood states, a Mott insulator and a BCS superconductor, yet neither state has as yet worked as a good starting point for understanding what lies between them. This thesis explores the doping and temperature dependence of the complex conductivity of a sample near the lower critical doping for superconductivity in order to elucidate some of what is occurring in the underdoped region of the phase diagram.
Chapter 2

Superconductivity

One of the defining characteristics of the superconducting state is the absence of dc electrical resistance below the critical temperature $T_c$ as first discovered by Onnes [5] in 1911, and was thought to result from a disappearance of scattering. After all, it was known that the resistance of metals dropped continuously from their room temperature value and if you extrapolated their temperature dependence to zero temperature, many of their intercepts would be negative. This thought prevailed until two other discoveries were made: in 1932 Keesom and Kok [44] measured a discontinuity at $T_c$ in the heat capacity of tin; and in 1933 Meissner and Ochsenfeld [45] observed the expulsion of magnetic flux below $T_c$. Together these measurements indicated a phase transition had occurred and the electrons had ordered into a new ground state. The Meissner state was first successfully described in 1935 by London and London [46], but a full theory of the superconducting state did not arrive until 1957 when Bardeen, Cooper and Schrieffer [6] realized that electrons must pair up to form a boson known as a Cooper pair in the superconducting state.

2.1 London theory

Although the theory of London and London [46] was superceded by the microscopic BCS theory, it remains a good starting point for describing the electrodynamics of the superconducting state. The following derivation follows those of Waldram [47] and Tinkham [48].
We start with the Schrödinger equation for an electron in a magnetic field,
\[
\left[ \frac{1}{2m} (-i\hbar \nabla + eA)^2 - e\phi \right] \Psi = E \Psi,
\] (2.1)
where \(m\) and \(e\) are the electron mass and charge, respectively, \(A\) is the magnetic vector potential, \(\phi\) the electric potential and \(\Psi\) the superconducting wave function. In this formalism the supercurrent density takes the form
\[
J_s = \frac{ie\hbar}{2m} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) - \frac{e^2}{m} \Psi \Psi^* A.
\] (2.2)
In the superconducting state it is assumed that the amplitude of the wave function does not vary in space, but that the phase may vary. Thus the wave function \(\Psi\) is written in terms of its amplitude and phase as \(\sqrt{n_s} e^{i\vartheta}\); i.e. it is normalized to a pair density \(n_s\). With this wave function, Equation 2.2 reduces to
\[
J_s = -n_s e^2 \left( \frac{\hbar}{2e} \nabla \vartheta + A \right).
\] (2.3)
This equation contains much of the essential physics of the superfluid.

The first London equation can be derived by taking the time derivative of Equation 2.3 as follows:
\[
\frac{\partial J_s}{\partial t} = -n_s e^2 \left( \frac{\hbar}{2e} \frac{\partial \nabla \vartheta}{\partial t} + \frac{\partial A}{\partial t} \right).
\] (2.4)
The next step is to realize that the time derivative of the phase of the pair wave function is related to the local pair energy which is equal to twice the electrochemical potential \(\mu\). Thus
\[
\hbar \frac{\partial \vartheta}{\partial t} = -2\mu.
\] (2.5)
Inserting Equation 2.5 into Equation 2.4 yields
\[
\frac{\partial J_s}{\partial t} = \frac{n_s e^2}{m} \left( \frac{\nabla \mu}{e} - \frac{\partial A}{\partial t} \right).
\] (2.6)
If we then recall that electrons flow in response to the gradient of the electrochemical potential \(\mu\) rather than the gradient of \(\phi\) then the terms enclosed by brackets on the right hand
side of Equation 2.6 can be replaced by an effective electric field $E_{\text{eff}}$ yielding the first London equation

$$\frac{\partial J_s}{\partial t} = \frac{n_s e^2}{m} E_{\text{eff}}. \quad (2.7)$$

This equation is an acceleration equation for the superfluid, implying that after a short pulse of electric field the system will be left with a supercurrent which will not decay, i.e. perfect conductivity.

Taking the curl of Equation 2.3 and remembering that the curl of a gradient is always zero leads to the second London equation:

$$\nabla \times J_s = -\frac{n_s e^2}{m} B. \quad (2.8)$$

This equation can be viewed as the supercurrent equivalent of Ohm’s law; it shows that the steady supercurrent is a function of the magnetic rather than electric field. $J_s$ can be replaced in Equation 2.8 using Ampère’s law $\nabla \times B = \mu_0 J_s$, giving

$$\nabla \times \nabla \times B = -\frac{\mu_0 n_s e^2}{m} B, \quad (2.9)$$

where $\mu_0$ is the permeability of free space. This can be simplified by remembering that $\nabla \times \nabla \times B = \nabla (\nabla \cdot B) - \nabla^2 B$ and that $\nabla \cdot B = 0$. Thus

$$\nabla^2 B = \frac{B}{\lambda^2}, \quad (2.10)$$

where $\lambda = \sqrt{m/\mu_0 n_s e^2}$ is the London penetration depth. This result is a screening equation for the magnetic field, implying that magnetic fields decay exponentially with depth as $e^{-r/\lambda}$ in a superconductor. The London penetration depth might not be isotropic, but rather may vary with direction, which it does in the cuprates due to their layered structure. The nature of the penetration depth in anisotropic materials is further discussed in Appendix A.

### 2.2 Ginzburg-Landau theory

Another theory of superconductivity was developed by Ginzburg and Landau in 1950 [49] and was shown to be a limiting form of BCS theory by Gor’kov in 1959 [50]. In Ginzburg-
Landau theory a complex wave-function $\psi$ is introduced as an order parameter within Landau’s general theory of second-order phase transitions. This wave-function describes the superconducting electrons and is related to their density such that

$$n_s = |\psi(x)|^2.$$  \hfill (2.11)

The Ginzburg-Landau theory of superconductivity uses the variational principle and an assumed series expansion of the free energy in powers of $\psi$ and $\nabla \psi$ with coefficients $\alpha$ and $\beta$ to derive the following differential equation for $\psi$:

$$\frac{1}{2m} \left( \frac{\hbar}{i} \nabla - eA \right)^2 \psi + \beta |\psi|^2 \psi = -\alpha(T) \psi.$$  \hfill (2.12)

This is analogous to the Schrödinger equation for a free particle, but with a nonlinear term. The corresponding equation for the supercurrent is also the same as the quantum-mechanical expression for current in the London theory (Equation 2.2).

### 2.3 Coherence length

Ginzburg-Landau theory introduces the Ginzburg-Landau coherence length

$$\xi(T) = \frac{\hbar}{|2m\alpha(T)|^{1/2}}$$  \hfill (2.13)

which characterizes the distance over which $\psi(r)$ can vary without undue energy increase. The coherence length can be interpreted in two different ways: it gives the approximate size of a Cooper pair; and it sets the length scale for variations in the superconducting order parameter. Pippard first argued for a characteristic dimension $\xi_0$ based on the uncertainty principle [51]. He argued that only electrons within $\sim k_B T_c$ of the Fermi energy can play a role in a phenomenon that occurs at $T_c$. These electrons have a momentum range $\Delta p \sim k_B T_c/v_F$, where $k_B$ is Boltzmann’s constant and $v_F$ is the Fermi velocity. By the uncertainty principle they then also have a spacial range

$$\Delta x \gtrsim \frac{\hbar}{\Delta p} \approx \frac{\hbar v_F}{k_B T_c}$$  \hfill (2.14)
leading to the definition
\[ \xi_0 = a \frac{\hbar v_F}{k_B T_c} \]  \hspace{1cm} (2.15)

where \( a \) is a numerical constant of order unity that evaluates to \( \sim 0.18 \) in BCS theory. In a pure superconductor far below \( T_c \) the Ginzburg-Landau coherence length is approximately equal to the Pippard coherence length. However, near \( T_c \) the Ginzburg-Landau coherence length diverges as \( (T_c - T)^{-1/2} \).

### 2.4 The two-fluid model

The discussion presented above neglects the effect of dissipative charge carriers. At finite frequencies the quasiparticle excitations of the superconductor constitute a normal fluid that conducts in parallel with the supercurrent. This leads to a conductivity that has both reactive and resistive contributions, i.e.

\[ \sigma = \sigma_1 - i\sigma_2. \]  \hspace{1cm} (2.16)

We have effectively already seen the conductivity of the superfluid in the time domain in the first London equation. Taking the Fourier transform of Equation 2.7 yields

\[ i\omega J_s(\omega) = \frac{n_s e^2}{m} E(\omega). \]  \hspace{1cm} (2.17)

Thus the imaginary part of the superfluid conductivity is

\[ \sigma_2(\omega) = \frac{n_s e^2}{m\omega}. \]  \hspace{1cm} (2.18)

Since the conductivity is a causal response function, its real and imaginary parts are related by a Kramers-Krönig transform. Thus the real part of the superfluid conductivity that arises as a result of the first London equation is found by taking the Kramers-Krönig transform of Equation 2.18:

\[ \sigma_1(\omega) = \pi \frac{n_s e^2}{m} \delta(\omega). \]  \hspace{1cm} (2.19)
CHAPTER 2. SUPERCONDUCTIVITY

The causality of the conductivity implies the oscillator-strength sum rule which states that the total area under $\sigma_1(\omega)$, or the total conductivity spectral weight, is a constant related to the total number of charge carriers $n$, i.e.

$$\frac{2}{\pi} \int_{0}^{\infty} \sigma_1(\omega) d\omega = \frac{n e^2}{m}. \quad (2.20)$$

Then, if we assume the total number of charge carriers is temperature independent, as should be the case at low temperatures in a metallic system, the sum rule implies that the total electron density $n$ is partitioned into a superfluid density $n_s$ and a normal-fluid density $n_n = n - n_s$. In this case, the conductivity can be written in terms of the dissipative and reactive contributions of the normal and super currents as

$$\sigma(\omega, T) = \sigma_1 S - i \sigma_2 S + \sigma_1 N - i \sigma_2 N$$

$$= \frac{n_s e^2}{m} \delta(\omega) - i \frac{n_s e^2}{m \omega} + \sigma_1 N - i \sigma_2 N. \quad (2.21)$$

The superfluid density $n_s$ is determined phenomenologically from measurements of the magnetic penetration depth $\lambda$ via the second London relation (Equation 2.10). Thus, at finite frequencies the conductivity can be written as

$$\sigma(\omega, T) = \sigma_1 N(\omega, T) - i \left[ \sigma_2 N(\omega, T) + \frac{1}{\mu_0 \omega \lambda^2(T)} \right]. \quad (2.22)$$

The normal, or quasiparticle, contribution to the conductivity is more complicated than that of the superfluid as it contains information about both the quasiparticle excitation spectrum and the quasiparticle charge dynamics. It has been shown using the self-consistent $t$-matrix approximation that the quasiparticle conductivity in a $d$-wave superconductor is well approximated by a simple, energy-averaged Drude form [52]

$$\sigma(\omega, T) = \frac{e^2}{m} \int_{-\infty}^{\infty} N(E) \left[ - \frac{\partial f(E)}{\partial E} \right] \frac{1}{i \omega + 1/\tau(E)} dE, \quad (2.23)$$

where $1/\tau(E)$ is an energy-dependent transport relaxation rate, $N(E)$ is the density of states, and $f(E)$ is the Fermi function at temperature $T$. It has further been shown by Turner et al. [53] that the conductivity spectra in some of the cuprates (e.g. ultraclean
Figure 2.1: (a) In the clean limit, the superconducting gap $2\Delta$ is larger than the scattering rate $1/\tau$ and most of the spectral weight condenses into the superfluid. (b) In the dirty limit $2\Delta \ll 1/\tau$ and only a fraction of the spectral weight is condensed. In both cases shown here the light grey represents the condensed spectral weight, while the dark grey represents the uncondensed. A peak at low frequencies may exist even at zero temperature, as shown in (b), if there is significant pair-breaking due to disorder.

YBa$_2$Cu$_3$O$_{6+x}$) are well described by a simple phenomenological form

$$\sigma_{1N}(\omega, T) = \frac{\sigma_{dc}}{1 + (\omega/\tau)^y}.$$  \hspace{1cm} (2.24)

where $y$ typically ranges from $\approx 1.4$ to $\approx 1.7$. For $y = 2$ we recover the familiar Drude form of a single Lorentzian. Reducing $y$ below 2 increases the upwards curvature at lower frequencies and increases the correspondence to the expected form for a $d$-wave superconductor with energy-dependent scattering. Also note that $y$ must be greater than one or the spectrum cannot be integrated, breaking the conductivity sum rule of Equation 2.20.

Inserting the quasiparticle conductivity of Equation 2.24 into Equation 2.22 gives us the total conductivity in the superconducting state at finite frequencies,

$$\sigma(\omega, T) = \frac{ne^2}{m} \left\{ \frac{f_s}{i\omega} + \frac{y\sin(\pi/y)\tau f_n}{2} \left[ \frac{1}{1 + (\omega/\tau)^y} - i\text{KK}\left(\frac{1}{1 + (\omega/\tau)^y}\right) \right] \right\}.$$ \hspace{1cm} (2.25)

Here KK($x$) represents the Kramers-Krönig transform of $x$. The prefactor of the quasiparticle conductivity term is obtained by insisting that the integral of Equation 2.24 over
CHAPTER 2. SUPERCONDUCTIVITY

frequency
\[
\int_0^\infty \frac{\sigma_{dc}}{1 + (\omega \tau)^y} \omega \, d\omega = \frac{\sigma_{dc}}{\tau} \frac{\pi}{y \sin(\pi/y)}
\]  
(2.26)

be independent of \(y\) and equal to \((\pi/2)f_n ne^2/m\), as required by the oscillator-strength sum rule. In the limit \(y = 2\), Equation 2.25 reduces to the result for the standard Drude two fluid model

\[
\sigma(\omega) = \frac{ne^2}{m} \left[ f_s + \frac{f_n}{1/\tau + i\omega} \right].
\]  
(2.27)

In this limit there are closed form expressions for the relaxation rate and the normal fluid fraction

\[
\frac{1}{\tau} = \omega \frac{\sigma_0 - \sigma_2(T)}{\sigma_1(T)},
\]  
(2.28)

\[
f_n = (1 + \omega^2 \tau^2) \frac{\sigma_0 - \sigma_2(T)}{\sigma_0},
\]  
(2.29)

where \(\sigma_0 = ne^2/m\) is the total conductivity spectral weight which may differ from \(\sigma_2(T \to 0)\) due to the pair-breaking effects of disorder. For \(y \neq 2\) no closed form expressions exist for the relaxation rate or normal fluid fraction, so Equation 2.25 must be inverted numerically to obtain \(1/\tau(T)\) and \(f_n(T)\).

In the superconducting state a gap of width \(2\Delta\) opens up in the conductivity spectrum. In the clean limit, where the width of the conductivity spectrum \(1/\tau\) is much less than the superconducting gap, most of the spectral weight collapses into the superfluid delta function, as illustrated in Figure 2.1a. The dirty limit, however, where \(1/\tau \gg 2\Delta\), is more complicated. In this case only a small fraction of the total spectral weight condenses into the superfluid and at zero temperature we are left with the situation shown in Figure 2.1b. The light grey area represents the amount of spectral weight that condenses into the superfluid and the peak at low frequency is due to the pair-breaking effects of disorder, which result in a residual density of states at zero temperature. A two fluid analysis can still be performed in the dirty limit, but with the knowledge that \(\sigma_2(T \to 0)\) does not represent the total spectral weight, but rather just the condensed spectral weight. However, in this case the condensed spectral weight is drawn from a region that is roughly rectangular (see Figure 2.1b), with area \(n_s e^2/m\), height \(\sigma_{dc}\) and width \(2\Delta\). Thus the magnitude of the superconducting gap can
be estimated from
\[ 2\Delta \approx \frac{\hbar \omega \sigma_2(T \to 0)}{\sigma_{dc}}. \]  
(2.30)

In our experiments we measure both the real and imaginary parts of the conductivity, and so we can estimate the magnitude of the gap provided we are in the dirty limit.

### 2.5 Microwave surface impedance

When measuring the response of a conducting surface at microwave frequencies, and irrespective of the internal dynamics of the conductor, the experimentally accessible quantity is the surface impedance \( Z_s \). The surface impedance is defined as the ratio of the tangential components of the electric and magnetic fields at the surface. For a surface in the \( x-y \) plane, and an r.f. magnetic field applied along the \( y \) direction,

\[ Z_s = \frac{E_x}{H_y} = R_s + iX_s. \]  
(2.31)

The surface resistance \( R_s \) is directly proportional to the power absorbed in the sample while the surface reactance \( X_s \) describes the inductive response. If the electromagnetic response is local (i.e. if the mean free path is much shorter than the penetration depth and the penetration depth is much longer than the coherence length) then \( Z_s \) is related to the complex conductivity in a straightforward manner via the expression

\[ Z_s = R_s + iX_s \equiv \sqrt{\frac{i\omega\mu_0}{\sigma}}. \]  
(2.32)

In metallic samples the transport scattering rate is typically much larger than the measurement frequency and the conductivity is predominantly real (\( \sigma_1 \gg \sigma_2 \)). This is the normal skin effect regime for a metal, which is characterized by the real and imaginary part of the surface impedance being equal and proportional to the square root of the dc resistivity \( \rho \), i.e.

\[ R_s \approx X_s \approx \sqrt{\omega\mu_0 \rho / 2}. \]  
(2.33)

The equality of \( R_s \) and \( X_s \) allows them to be matched in the normal state, which in turn allows the absolute value of the penetration depth to be determined in the superconducting...
In the superconducting state the superfluid response usually quickly dwarfs the dissipative response and over most of the temperature range $\sigma_2 \gg \sigma_1$. In this case the surface impedance can be approximated by

\begin{align}
R_s(\omega, T) &\approx \frac{1}{2} \mu_0^2 \omega^2 \lambda^3(T) \sigma_1(\omega, T), \\
X_s(\omega, T) &\approx \mu_0 \omega \lambda(T).
\end{align}

(2.34) (2.35)

Hence in the superconducting state, one finds that the surprising result that the surface resistance is proportional to the real part of the conductivity, while the surface reactance is proportional to the penetration depth.

### 2.6 BCS theory

The key idea behind the Bardeen, Cooper and Schrieffer theory of superconductivity is that of electrons experiencing an attractive interaction and forming Cooper pairs. The coupling of electrons to quantized lattice vibrations, or ‘phonons’, can lead to a small attractive interaction between electrons. This in turn pairs electrons of opposite momentum and spin, so that the pair can essentially be treated as a single charge carrier. However, Cooper pairs in a conventional BCS superconductor are spatially large, typically of order $10^{-6}$ m, and overlap strongly in space. Thus the binding turns out to be cooperative with all of the Cooper pairs locked into the same state. It is said that they have condensed into a macroscopic wavefunction somewhat analogous to a Bose-Einstein condensate. This condensation opens up a gap $2\Delta$ in the electronic density of states, i.e. in a conventional superconductor a minimum energy $2\Delta$ is necessary to break apart a Cooper pair. This gap opens up uniformly over the Fermi surface and is proportional to the Cooper pair wave function, which is isotropic in momentum space and has no angular momentum. This is similar to the $s$-shell of a hydrogen atom and thus is known as an $s$-wave gap. This uniformity of the gap in the density of states manifests itself as an exponentially activated temperature dependence for a number of physical properties, such as the penetration depth and the heat capacity.

While many superconductors are well explained by BCS theory and are thus called...
‘conventional’ superconductors, there are also a number of ‘unconventional’ superconductors that exhibit properties that are not fully explained by BCS theory. Despite this, useful insights about low-lying excitations can still be obtained from the weak-coupling BCS theory. For the case of an isotropic Fermi surface the temperature dependent penetration depth \( \lambda(T) \) is given by [47, 48]

\[
\frac{\lambda_0^2}{\lambda^2(T)} = 1 - \int_{-\infty}^{\infty} \left( -\frac{\partial f}{\partial \omega} \right) N(\omega) d\omega
\]

\[
= \frac{1}{2} \int_{-\infty}^{\infty} \text{tanh} \left( \frac{\omega}{2k_B T} \right) \frac{\partial N(\omega)}{\partial \omega} d\omega .
\]

Here \( \lambda_0 \) is the zero-temperature penetration depth in the absence of disorder and competing phases, and \( f(\omega/T) \) is the Fermi function. A Sommerfeld expansion reveals the direct connection between \( \lambda(T) \) and the normalized density of quasiparticle states \( N(\omega) \); if \( N(\omega) = N_0 + N_1 \omega + \frac{1}{2} N_2 \omega^2 + \ldots \) then \( \lambda_0^2/\lambda^2(T) = 1 - N_0 - 2 \ln 2 k_B T - \frac{\pi^2}{6} N_2 (k_B T)^2 - \ldots \).

The residual density of states \( N_0 \) represents zero-energy excitations, which may arise in a superconductor either from impurity pair-breaking, or from certain types of competing order. Note that \( N_0 \) does not appear in the temperature dependence of \( \lambda \), but instead results in a deviation of \( \lambda(T \to 0) \) from \( \lambda_0 \). This shift in penetration depth is difficult to resolve experimentally because \( \lambda_0 \) is neither known a priori, nor can the absolute value of \( \lambda(T \to 0) \) usually be measured with sufficient accuracy. However, a direct determination of \( N_0 \) can be obtained from the uncondensed spectral weight in the quasiparticle conductivity \( \sigma_1(\omega, T) \).

From the oscillator strength sum rule the residual density of states \( N_0 \) can be calculated:

\[
N_0 = \frac{2}{\pi} \mu_0 \lambda_0^2 \int_0^{\omega_c} \sigma_1(\omega, T \to 0) d\omega , \tag{2.38}
\]

where \( \omega_c \) is a frequency cut-off chosen to capture the oscillator strength of the conduction electrons only.

Within BCS theory there are two types of superconductors, fittingly called type-I and type-II. In a type-I superconductor the penetration depth is much smaller than the coherence length. This implies a positive surface energy associated with a domain wall between normal and superconducting material. In a type-II superconductor, however, the penetration depth is greater than the coherence length and the surface energy of a domain wall is
negative. Thus a type-I superconductor will resist the formation of pockets of superconducting and normal regions, while a type-II will subdivide into domains until the domains are reduced to a size of order the coherence length. The difference between type-I and type-II superconductors manifests itself in how they behave in an applied magnetic field. As applied magnetic field is increased, a type-I superconductor will expel magnetic flux from the interior of a sample until there is a discontinuous breakdown of superconductivity in a first-order transition at the critical field $H_c$. However, under the same circumstances in a type-II superconductor there is a continuous increase in the flux penetration starting at the lower critical field $H_{c1}$, and the total field in the sample equals the applied field at the upper critical field $H_{c2}$. 

Chapter 3

D-wave superconductivity in the cuprates

While BCS theory and s-wave pairing explain the properties of conventional superconductors like lead, tin and aluminum, they do not describe those of the cuprates. In conventional superconductors the pairing state has the same symmetry as the underlying crystal. While this means that the magnitude of the gap may have momentum dependence, only in exotic cases, such as extended s-wave, will the gap have nodes. In an unconventional superconductor, the symmetry of the gap function is lower than that of the crystal. In this case the gap will have a different sign on different parts of the Fermi surface, usually with a zero-crossing in between. The pairing state in the cuprates has been found to be unconventional, and a d-wave character has been confirmed, at least in the mid-underdoped to overdoped regime.

3.1 d-wave pairing

The first insight into the pairing state of the cuprates came from nuclear magnetic resonance measurements of the Knight shift, which showed that the spin susceptibility falls rapidly below $T_c$ [54, 55]. This indicates an absence of equal spin pairing and makes a spin-triplet, or p-wave, state unlikely. Therefore, the pair wave function is likely a spin-singlet state, with pairing in either an s-wave state or some higher, even angular momentum channel.
Figure 3.1: (a) The $d$-wave superconducting gap on a circular Fermi surface. The blue (red) portions represent the fact that the gap is positive (negative) in these regions. This change of sign on traversing the Fermi surface produces nodes in the gap function where quasiparticles can be excited out of the condensate at arbitrarily low energies. The dashed line represents an $s$-wave gap with the same maximum amplitude. (b) The energy dispersion near the $d$-wave node is shaped like a flattened cone (grey) as $v_F \gtrsim v_\Delta$. The density of states at a given energy is thus a banana-shaped arc (green). The red indicates filled states.

such as $d$-wave.

The $d$-wave state is quite different from the $s$-wave state. While the $s$-wave state is nearly isotropic, the $d$-wave state breaks four-fold rotational symmetry. The $d$-wave gap varies as $\Delta(\theta) \approx \Delta_0 \cos(2\theta)$, where $\theta$ measures the angle around a two-dimensional Fermi surface. Thus the $d$-wave state has four nodes in momentum space where the energy gap goes to zero as shown in Figure 3.1a. Near these nodes the quasiparticle spectrum has an anisotropic Dirac form, $\epsilon_p = \sqrt{v_F^2 p_\perp^2 + v_\Delta^2 p_\parallel^2}$, where $v_F$ is the Fermi velocity, $v_\Delta \equiv \frac{1}{p_\perp} \left| \frac{\partial \Delta(\theta)}{\partial(\theta)} \right|$ parameterizes the dispersion of the gap near the nodes and $p_\perp$ and $p_\parallel$ measure the momentum from the nodal point, perpendicular and parallel to the Fermi surface respectively. At these nodal points it is possible to produce excitations at arbitrarily low energies. In a clean limit BCS superconductor, the density of states is determined by the $k$-space structure of the superconducting order parameter $\Delta_k$: $N(\omega) = \Re \langle \omega / \sqrt{\omega^2 - \Delta_k^2} \rangle_{\text{FS}}$, where $\langle ... \rangle_{\text{FS}}$ denotes a Fermi surface average. Since the superfluid density is closely related to the density of states (recall Equation 2.37), this makes $\rho_s(T)$ a sensitive probe of order parameter symmetry. In particular, for a $d$-wave superconductor in two dimensions,
the linear dispersion of $\Delta_k$ about the gap nodes leads to $N(\omega) \propto \omega$ and $\Delta \rho_s(T) \propto T$. An $s$-wave superconductor, by contrast, usually has a finite energy gap and shows activated exponential behaviour, $\rho_s(T) \propto \exp(-\Delta_{\text{min}}/k_B T)$, where $\Delta_{\text{min}}$ is the minimum of the energy gap on the Fermi surface. The effect of impurity scattering on $N(\omega)$ and $\rho_s(T)$ is important and is reviewed in Appendix C, where analytic results are given for $d_{x^2-y^2}$, $d_{x^2-y^2} + id_{xy}$ and $d_{x^2-y^2} + is$ superconductors with isotropic Fermi surfaces in the presence of point defects. The end result is that: a $d_{x^2-y^2} + is$ state has an energy gap that is robust in the presence of defects, resulting in an exponential low-temperature temperature dependence of the superfluid density regardless of the defect level; a $d_{x^2-y^2} + id_{xy}$ state has an energy gap that is wiped out in the presence of defects, resulting in a crossover from exponential temperature dependence of the superfluid density in the absence of defects to a $T^2$ temperature dependence in the presence of defects; and a pure $d_{x^2-y^2}$ has no energy gap resulting in a $T$-linear temperature dependence of the superfluid density in the absence of defects and $T^2$ in their presence.

In the presence of a supercurrent, thermally excited quasiparticles generate an opposing paramagnetic back-flow current, decreasing the effective density of superfluid carriers, $n_s$. In a clean $d$-wave superconductor, nodal quasiparticles deplete the superfluid density, $\rho_s$, linearly with temperature [56]:

$$\rho_s(T) \equiv \frac{n_s(T)}{m^*} = \frac{n_s(0)}{m^*} - \frac{2}{\pi} \frac{k_B}{\hbar^2} \frac{1}{d} v_F \alpha^2 T, \quad (3.1)$$

where $m^*$ is the effective mass of the paired holes, $d$ is the average spacing of the CuO$_2$ layers, and $\alpha$ is the charge-current renormalization factor. Charge-current renormalization arises since the contribution of nodal quasiparticles to the superfluid density can be modified from the bare form expected from the simple Dirac spectrum [57–60]. This is usually taken into account by a new definition of the electrical current density: $j_{\text{bare}} = nev_F \rightarrow j_{\text{renorm}} = ne\alpha v_F$, resulting in the $\alpha^2$ that appears in Equation 3.1.

The linear temperature dependence of the superfluid density (see Figure 3.2) was first observed in measurements of the magnetic penetration depth of optimally-doped YBa$_2$Cu$_3$O$_{6.95}$ and provided some of the earliest evidence for unconventional superconductivity in the cuprates [61]. Similar measurements have since been used to probe the nature of the nodal quasiparticles at other hole dopings and in different materials [62, 63] and have...
confirmed the $d$-wave character of the penetration depth throughout the overdoped portion of the phase diagram and into the underdoped region down to dopings of about $p = 0.11$.

Further evidence for a $d$-wave superconducting state in the cuprates comes from ARPES measurements. The energy gap mapped out by ARPES near the Fermi energy is indeed consistent with 4 nodes in the gap function located along the zone diagonals, consistent with a $d_{x^2-y^2}$ state. The definitive evidence for a $d$-wave gap comes from a series of phase-sensitive measurements, where Tsuei et al. have shown that a $d_{x^2-y^2}$ pairing symmetry is robust over a large variation in doping [64–66].

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3.2 *c*-axis electrodynamics

When currents are induced to flow along the *c*-axis of cuprate samples the electrodynamics are somewhat different from what occurs for currents within the planes. This is due in part to the high anisotropy of the cuprate crystal structure (see Chapter 6). As a result currents flowing along the *c*-axis are Josephson tunnelling currents, as has been shown explicitly in a number of cuprate materials [67, 68]. An example of this Josephson tunnelling is shown in Figure 3.3, where a plot of the current versus voltage measured across a stack of 9 layers of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ shows 9 clear branches.

The Josephson tunnelling physics also affects the temperature dependence of the *c*-axis penetration depth as shown by Sheehy et al. [69] who developed a theory of the *c*-axis penetration depth and found excellent agreement with data on underdoped YBa$_2$Cu$_3$O$_{6+x}$ [69, 70]. The *c*-axis penetration depth is captured within a model of incoherent electron tunnelling between CuO$_2$ planes. Their results show that in the general case

$$
\delta \lambda_c(T) \equiv \frac{1}{\lambda^2(0)} - \frac{1}{\lambda^2(T)} \approx \frac{16e^2\Delta d}{\pi \hbar^4} \frac{t_\perp^2}{\sqrt{v_Fv_\Delta}} \left( \frac{T}{\sqrt{v_Fv_\Delta} \Lambda} \right)^\beta,
$$

where $t_\perp$ is an energy scale characterizing the strength of tunnelling, and $\Lambda$ is an inverse

---

length scale characterizing the degree of momentum nonconservation. Also note that $\beta$ may vary from 1 to 3 as a function of temperature, as a crossover from momentum-conserving to diffuse tunnelling occurs. Related results have previously been derived for specific cases: Radtke et al. [71] showed that in the limit momentum-conserving incoherent tunnelling $\delta\lambda_c(T) \propto T^2$; and Hirschfeld et al. [72] showed that in the diffuse tunnelling limit $\delta\lambda_c(T) \propto T^3$. 
Chapter 4

Fluctuations

In equilibrium, every degree of freedom in a classical system has thermal energy of order $k_B T$ at its disposal. In parallel with this, quantum mechanical uncertainty does not allow the state of a system to be specified more tightly than a quantum of action $\hbar$. We therefore need a description of the system that recognizes that it will fluctuate into low-lying states with a finite probability. Thus below $T_c$ fluctuations may produce a finite resistance at currents below the critical current, and above $T_c$ fluctuations cause some vestiges of superconductivity to remain and lower the resistance. These fluctuations can have a strong influence on measured properties, especially in the cuprates, due to their high $T_c$ and thus short coherence length, their layered structure, and their low superfluid density.

There are two important length scales in a superconductor: the coherence length $\xi_0$ and the penetration depth $\lambda$. While we have discussed the importance of the penetration depth in terms of shielding the interior of a superconductor from applied magnetic fields, it is also related to another important property of superconductors, namely the phase stiffness or superfluid density. The coherence length on the other hand sets the length scale for variations in the superconducting wave function. In the cuprates $v_F$ is $2.6 \times 10^5$ m/s [73] and $T_c$ is of order 100 K, leading to a zero temperature coherence length less than 10 nm. This small coherence length implies that the energy cost for creating small pockets of superconductor in the normal state, or small pockets of normal region in the superconducting state, is quite small, thereby markedly increasing the importance of fluctuations.


CHAPTER 4. FLUCTUATIONS

4.1 Phase stiffness and superfluid density

The superconducting wave function is $\psi = \sqrt{n_s} \exp(i\phi)$. The significance of variations in the phase of the wave function can be seen by considering the kinetic energy associated with the superfluid. The kinetic energy can be written as $n_s \left( \frac{1}{2} m v_s^2 \right)$ where the supercurrent velocity is given by

$$m v_s = p_s - eA = \hbar \nabla \phi - eA.$$  \hspace{1cm} (4.1)

In the absence of magnetic fields the kinetic energy density is then given by

$$\frac{\hbar^2}{2m} n_s (\nabla \phi)^2.$$  \hspace{1cm} (4.2)

Thus the scale of the energy cost for variations in the phase of the wave function is set by the superfluid density $n_s/m$. The superfluid density is also, therefore, known as the phase stiffness.

In standard BCS theory the transition temperature is determined solely by the amplitude of the order parameter and the phase is unimportant. However, when the the superconducting carrier density is low, as in the cuprates, there is a relatively small phase stiffness and poor screening. This implies a significantly larger role for phase fluctuations. Consequently, in underdoped material, the onset of long-range phase coherence controls the gross value of $T_c$ [74]. This is evidenced by the famous Uemura relation: $T_c \propto \rho_s(T = 0)$ [75]. Uemura et al. found a linear relationship between $T_c$ and the zero temperature superfluid density from their measurements of the muon-spin-relaxation rate in multiple cuprates. As a result of the early observation of the empirical Uemura relation, there have been many suggestions [74, 76–81] that the superconducting transition in the underdoped cuprates is a phase-disordering transition and that the pseudogap state above $T_c$ is a phase-disordered $d$-wave superconductor. Another piece of evidence for a phase-disordering transition is the dichotomy that as doping is reduced, both $\rho_s$ and $T_c$ decline while the maximum energy gap $\Delta_0$ increases. Further evidence for superconductivity above $T_c$ has come from experiments suggesting magnetic vortices [31], strong fluctuation diamagnetism [33], and fermionic nodal quasiparticles [82] in the pseudogap state. In addition, one would expect a phase-disordering transition to have a wide critical region and be in the 3D-$XY$ universality class as is seen in a number of experiments [83–85].
More recent measurements on thin films of YBa$_2$Cu$_3$O$_{6+x}$ show approximately a square root dependence of transition temperature on zero-temperature superfluid density, $T_c \propto \rho_{s0}^{1/2}$ [86], while measurements on ultra-thin films of Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ show a crossover from approximately $T_c \propto \rho_{s0}^{1/2}$ at higher doping to $T_c \propto \rho_{s0}$ at low doping [87].

### 4.2 Two-dimensionality

The cuprates are very anisotropic, with many properties differing by two to four orders of magnitude between in-plane and out-of-plane. This weak coupling between the superconducting layers means that the cuprates are often treated as though they were two dimensional. The problem with this treatment is that in two dimensions the Mermin-Wagner theorem states that systems with a continuous degree of freedom can only have a phase transition at $T = 0$. In the case of a superconductor the phase of the order parameter would become incoherent and the system would appear to lose its superfluid properties [47].

In thin films, another nearly two dimensional system, it is well known that as the temperature is raised a Kosterlitz-Thouless vortex unbinding transition occurs at $T_{KT} < T_c$. This is because in a thin film the entropy gained by producing a vortex-antivortex pair outweighs the energy cost. Formally, the Kosterlitz-Thouless transition temperature is defined by

$$k_B T_{KT} = \frac{\pi \hbar^2 d}{8e^2 \mu_0 \lambda_{eff}^2(T_{KT})},$$

where $d$ is the thickness of the film and $\lambda_{eff} \approx \lambda_0 \sqrt{\xi_0 / d}$ is the effective penetration depth in a thin film. If the interlayer coupling in the cuprates is low enough then the planes may act independently and it is possible that a Kosterlitz-Thouless transition will occur in bulk samples.

### 4.3 Paraconductivity

Above $T_c$, fluctuation-induced Cooper pairs will carry current in parallel with the normal electrons resulting in a reduction of the resistivity near $T_c$. This reduction of the resistivity or enhancement of the conductivity is referred to as the paraconductivity or excess conductivity.
The theoretical temperature dependence of the excess conductivity was first calculated by Aslamazov and Larkin [88] and in three dimensions is

$$\sigma_{AL} = \frac{e^2}{32\hbar\xi_0} \left( \frac{T}{T - T_c} \right)^{\frac{1}{2}},$$

(4.4)

where $\xi_0$ is the coherence length. In a film thin enough to justify a two-dimensional approximation, i.e., one in which the thickness $t \ll \xi_0$, the result is similar:

$$\sigma_{AL} = \frac{e^2}{16\hbar t} \frac{T}{T - T_c}.$$

(4.5)

These two formulas showed remarkable agreement with early experimental results [89]. In layered systems like the cuprates one would expect a crossover to occur between two-dimensional behaviour well above $T_c$ and three-dimensional behaviour near $T_c$. Lawrence and Doniach [90] first predicted and developed the theory of a dimensional crossover as a function of temperature for thin film superconductors, although in the case of thin films the crossover is from three-dimensional well above $T_c$ to two-dimensional near $T_c$. Their theory can be modified for the cuprates to give

$$\sigma_{LD} = \frac{e^2}{16\hbar t} \left[ \left( \frac{T - T_c}{T} \right)^2 + \left( \frac{2\xi}{t} \right)^2 \right]^{-\frac{1}{2}}.$$

(4.6)

Soon after Aslamazov and Larkin’s theory was found to work in some materials, other materials were found to display paraconductivities that were much larger that the Aslamazov-Larkin (AL) result [91]. This was explained theoretically when Maki [92] noted the existence of another term in the theoretical calculation that had been omitted by AL. In two dimensions, however, this "Maki term" predicts an infinite conductivity at all temperatures above $T_c$. This nonphysical divergence can be prevented by the addition of any pair-breaking, as shown by Thompson [93]. The addition of this Maki-Thompson (MT) term to the AL result can account for much experimental data.

A full calculation of the excess conductivity in a layered material was performed by Dorin et al. [94]. They included contributions from the AL and MT terms as well as from fluctuations in the quasiparticle density of states (FDOS). There are three free parameters in
the Dorin theory. There is $J$, which is an effective quasiparticle nearest-neighbour interlayer hopping energy, $1/\tau$ is a scattering rate, and $\tau_\phi$ is a phase pair-breaking lifetime. It is expected that the scattering rate is larger than the phase pair-breaking rate. Their theory successfully accounts for the excess conductivity seen both parallel and perpendicular to the copper-oxygen planes in many of the cuprates [95]. In Chapter 8 we will discuss attempts to fit a number of the above mentioned theories to our measured paraconductivity.
Chapter 5

Experimental methods

Our measurements of complex surface impedance are performed using microwave cavity perturbation techniques. Measurements at microwave frequencies are especially useful for superconductors, where the d.c. resistivity is shorted to zero by supercurrents. At microwave frequencies the conductivity of a superconductor remains finite, but with a large out-of-phase component due to the purely reactive response of the super-electrons. Microwave measurements are often able to couple to both of these components.

This chapter will describe cavity perturbation, our apparatus, and the method we use to extract the surface impedance from measurements of resonant frequency and bandwidth.

5.1 Overview of cavity perturbation

The complex surface impedance can, in principle, be obtained from an optical-type reflectivity experiment. In practice, however, this is extremely difficult because in good metals and superconductors the reflectivity at microwave frequencies is indistinguishable from unity, and the sample size is often comparable to the wavelength, making diffraction effects important. The low frequency approach of attaching leads directly to the sample is also problematic. This is because the impedance is typically a fraction of an ohm, which is comparable to the contact resistance, and is difficult to match to the characteristic impedance of a microwave transmission line.

Cavity perturbation techniques are able to circumvent many of these problems. In cavity perturbation the sample is treated as part of the inner surface of a high quality factor
(high-$Q$) resonator, often a superconducting cavity. The resonator amplifies the interaction of the electromagnetic radiation with the sample by the $Q$ factor, through repeated reflection of the fields. This multiplies up the signal and provides effective impedance matching to transmission lines. As a result, the resolution of the experiment improves with the $Q$ of the resonant mode, allowing the properties of very low loss samples to be measured. The resonator also creates fields that are spatially well defined, simplifying geometric effects that arise in the diffraction limit. Early cavity perturbation techniques involved producing a cavity made entirely of the material to be studied. However, the cuprate superconductors are ceramic materials and the best quality samples tend to be small single crystals, often less than a millimetre in size. This makes constructing entire resonators out of cuprate material challenging. It also means that, in real measurement systems, the samples make up a very small portion of the area of the resonator walls. When coupled with their low microwave absorption, this makes them very difficult to perform measurements on. One of the innovations adopted to address these issues is the sapphire hot-finger technique [96] which allows the sample to be heated independently of the resonator. This allows the resonator temperature to be held constant for the duration of the experiment. This allows all changes in frequency and bandwidth can be attributed to the sample’s surface impedance as its temperature is varied.

While many microwave cavities are built out of superconducting materials, our resonators make use of dielectrics housed inside of a copper enclosure. Though superconducting resonators are able to produce very high quality factors, often order of $10^{10}$, they have a number of limitations. For example, any joints in the structure tend to act as superconducting weak links, limiting operation to low power. The quality of superconducting resonators also degrades over time due to oxidation of the surface. Also, superconducting resonators cannot be used in high magnetic fields as they would either be driven normal or into a highly dissipative state of flux flow. To this end our group has developed a number of dielectric resonators fabricated from oriented single crystals of rutile-phase TiO$_2$. Rutile was chosen as the dielectric material because of its high dielectric constant, $\epsilon_r \approx 120$, and its low loss tangent, $\tan \delta \approx 3 \times 10^{-8}$. For high $\epsilon_r$ material, displacement currents are very efficient at confining the microwave fields, reducing the magnitude of lossy conduction currents in the walls of the resonator enclosure. This, combined with the low loss tangent, results in quality factors well in excess of a million.
Figure 5.1: Cut-away schematic of the low temperature end of the microwave magnetic probe. Cavity perturbation is carried out using a rutile resonator at a frequency of 2.64 GHz.

### 5.2 Cavity perturbation apparatus

The main piece of apparatus used for cavity perturbation was the microwave magnetic field probe (MMP). The MMP is a dielectric cavity resonator designed and built by Drs. D. Broun and W. Hardy at the University of British Columbia. It uses a helium bath and a 1 K pot to access temperatures from 1.2 K to 300 K and can be used in high magnetic fields. One cavity perturbation experiment was also performed using a dielectric cavity resonator mounted in a dilution refrigerator. This apparatus was designed and built by Drs. P. Turner and D. Broun at Simon Fraser University and can access sample temperatures from 50 mK to 35 K.
Figure 5.1 shows an IronCAD rendering of the low temperature end of the microwave magnetic field probe. A dielectric resonator made of a single crystal of TiO$_2$ in the rutile phase is mounted on a sapphire disk in the center of a copper enclosure. The use of a copper enclosure rather than a superconducting one allows measurements to be performed in strong magnetic fields. The rutile cylinder has a diameter of 10 mm and a height of 10 mm, which produces a TE$_{011}$ resonance at 2.64 GHz. The sample is mounted on a sapphire hot finger that allows us to control the sample temperature independently of the temperature of the resonator, greatly reducing thermal drift. The hot finger is connected via a quartz tube, which acts as a weak thermal leak to a 1K pot. This entire thermal assembly is movable via a room temperature drive, allowing us to completely remove the sample and sapphire rod from the resonator to measure the background bandwidth of the resonance and thereby determine the absolute change in bandwidth. The length of the sapphire rod is chosen such that the sample is positioned at an antinode in the microwave magnetic field when the drive rod fully engaged. The structure of the microwave magnetic field produced by two useful resonant modes is shown in Figure 5.2. The sample is situated in a region of approximately uniform field, at a turning point in the standing wave pattern, allowing control over the plane in which currents flow in response to the applied microwave field.
5.3 Cavity perturbation theory

Cavity perturbation is a method for relating changes in the free response of a high-$Q$ resonator to changes in: the surface impedance $Z_s$; the permittivity $\epsilon$; and the permeability $\mu$, of small samples placed inside the cavity. The main cavity perturbation result [1, 97, 98] is:

$$\Delta f_0 + i \Delta f_B / 2 \approx \left\{ \frac{i}{2\pi} \int_S \Delta Z_s H_1 \cdot H_2 dS - f_0 \int_V \left[ \Delta \mu H_1 \cdot H_2 + \Delta \epsilon E_1 \cdot E_2 \right] dV \right\} / 4U$$

(5.1)

where $\Delta f_0$ and $\Delta f_B$ are the perturbative shifts in the resonant frequency and half-power bandwidth, respectively, $U$ is the electromagnetic energy stored in the resonator, $S$ and $V$ are the surface and volume of the resonator, respectively, $E$ and $H$ are complex phasor amplitudes of the electromagnetic fields, and the subscripts 1 and 2 denote the configurations before and after the perturbation.

In our experiments the perturbation is caused by the presence of the sample and sapphire hot-finger, and is due to either a shift in sample position or temperature. A large frequency shift occurs when the sample is inserted into the resonator, which prevents us from measuring the absolute frequency shift directly. This frequency shift is due to the volume of the sample and the non-unity dielectric constant of the sapphire rod. However, since the sapphire rod has very low loss and the sample volume does not affect $\Delta f_B$, the absolute bandwidth shift can be measured directly. This is done by comparing the bandwidth of the empty resonator to the bandwidth with the sample in position. With the sample positioned at the center of the resonator we can then vary its temperature. Since there are no further changes to the permeability or permittivity of the resonator, we can ignore the volume integral in Equation 5.1 and the cavity perturbation formula reduces to

$$R_s(T) + i \Delta X_s(T) \approx \Gamma [\Delta f_B(T)/2 - i \Delta f_0(T)]$$

(5.2)

where $\Gamma = 8\pi U / \int_S H_1 \cdot H_2 dS$ is the resonator constant.
5.4 Experimental uncertainties

When performed correctly, the cavity perturbation method is capable of measuring surface impedance of small single crystals with low uncertainty. Cavity perturbation is essentially a ratiometric technique — the effect of the sample on the cavity is implicitly being compared with the effect of a reference sample of known surface impedance, and of similar geometry. In a well-functioning experimental setup, random errors in the measurement of the bandwidth and centre frequency can be controlled and reduced to insignificant levels by the signal-averaging ability of the modern microwave network analyser. As a result, in most instances the random error in the raw surface impedance data presented here is usually smaller that the size of the data point. This then leaves the issue of systematic uncertainties in the determination of absolute surface impedance. Since these depend finally on comparison with a reference sample, the absolute uncertainty comes down to two things: how well the surface impedance of the reference sample is known; and the extent to which the geometries of the test and reference sample are different and/or can be related. On the first point, our reference samples are usually made from Pb or Pb/Sn material for which the resistivity is known to 2.5%. The second point, concerning geometry, can lead to larger uncertainties, especially for irregularly shaped samples. However, the samples used in these experiments are approximately spherical, allowing their size to be inferred from their mass to an accuracy of about 2% and the sphere area to 4%. Combining these uncertainties in quadrature leads to an overall uncertainty of about 6% in the overall scale of the surface impedance. It should be pointed out that this uncertainty applies the data set as a whole, while the doping to doping uncertainty is much smaller as the same sample was used throughout.
Chapter 6

The Sample

YBa$_2$Cu$_3$O$_{6+x}$ is unique among the cuprate superconductors for a number of reasons: its high stability relative to other chemical phases mean that it can be grown in single crystal form with cation disorder less than one part in $10^4$ \cite{99}; the oxygen content of a crystal can be adjusted through annealing in such a way that half of the superconducting dome can be accessed; and the oxygen atoms in the chain layer remain mobile at temperatures close to room temperature. The low level of cation disorder allows for the study of intrinsic physics with minimal complications from the contribution of defects, which is a major problem with most other cuprates, and the ability to control oxygen content allows for systematic studies across the entire YBa$_2$Cu$_3$O$_{6+x}$ phase diagram. Perhaps the most interesting and useful quality of highly underdoped YBa$_2$Cu$_3$O$_{6+x}$, however, is the mobility of the chain layer oxygen atoms, a property that no other cuprate has. As a result there are two methods of controlling doping in YBa$_2$Cu$_3$O$_{6+x}$: changing the overall oxygen content; and changing the ordering of oxygen atoms in the chain layer. This second method allows us to study doping dependence in a single sample with no change in either the cation disorder or the amount of oxygen in the sample.

6.1 Crystal structure and oxygen ordering

The crystal structure of fully oxygenated YBa$_2$Cu$_3$O$_7$ is shown in Figure 6.1. The unit cell of YBa$_2$Cu$_3$O$_{6+x}$ contains two CuO$_2$ planes, which is where the superconductivity occurs, and a single CuO chain layer that acts as a charge reservoir. The two CuO$_2$ layers are
Figure 6.1: The crystal structure of fully oxygenated YBa$_2$Cu$_3$O$_{6+x}$. There are two CuO$_2$ planes per unit cell and one CuO chain layer that acts a charge reservoir.
Figure 6.2: The dopings indicated by the large blue dots are "special" oxygen contents at which the oxygen atoms in the chain layers can be ordered into extremely long chains, producing samples that are highly ordered.

Separated by an yttrium layer, and this sandwich is in turn separated from the chain layers by two BaO$_2$ layers. The resulting crystal structure is highly anisotropic with the $c$-axis lattice parameter being about three times larger than that of the $a$-axis (11.83 Å versus 3.86 Å). In addition, there is very little orbital overlap in the $c$-axis direction — the orbitals lie mostly in the $ab$-plane. This also contributes to large anisotropy in the transport properties of the material.

Optimal doping, where $T_c$ is highest in YBa$_2$Cu$_3$O$_{6+x}$, occurs at an oxygen content of 6.95 and corresponds to a $T_c$ of 93.5 K. YBa$_2$Cu$_3$O$_{6+x}$ can only be overdoped slightly, but can be underdoped past the critical doping for superconductivity. At higher doping levels YBa$_2$Cu$_3$O$_{6+x}$ is orthorhombic with dopant oxygen atoms preferentially situated along the $b$-axis. There are several "special" oxygen contents at which the oxygen can be or-
Figure 6.3: Illustration of dopant oxygen ordering in the CuO chain layers of YBa$_2$Cu$_3$O$_{6.333}$. For $T \gg 150^\circ$C the material is tetragonal and oxygen atoms occupy $a$- and $b$-axis sites with equal likelihood. Below $T \approx 150^\circ$C the material adopts the Ortho-I structure, with oxygen randomly distributed amongst $b$-axis sites. Hole doping is very low in this phase and samples are not superconducting. Upon annealing at room temperature for 3 to 6 weeks, the oxygen orders into the Ortho-II structure, with every second chain empty, and $T_c$ becomes small but finite. High hydrostatic pressure ($p > 25$ kbar) promotes further ordering at room temperature, and is believed to induce the Ortho-III' phase, with a maximum $T_c$ near 20 K.

The sample studied in this work has the chemical formula YBa$_2$Cu$_3$O$_{6.333}$. As grown the distribution of dopant oxygen atoms will be random, along both the $a$- and $b$-axis, in what is known as the tetragonal phase [100, 101]. Upon cooling to room temperature the dopant oxygen atoms preferentially enter $b$-axis positions, a configuration known as a partially filled Ortho-I phase (shown in Figure 6.3), and the sample becomes orthorhombic, but not
superconducting. If the sample is allowed to sit at room temperature, dopant oxygen atoms enter a partially filled Ortho-II phase (also shown in Figure 6.3) with every other chain empty and $T_c$ will rise to between 2 and 3 K. At this point high pressure annealing can be used to further increase the dopant coordination and increase $T_c$. In theory, high pressure annealing should be able to produce a phase known as Ortho-III′, where every third chain is full while the other two remain empty. Until now, however, there is no diffraction evidence for this phase, although the associated superlattice Bragg peak is expected to be very weak, in part because of a tendency for such an order to contain antiphase domain walls.

The nature of the hole doping process can be illustrated as in Figure 6.4 [100, 101]. An empty chain layer will have all of its copper atoms in the Cu$^{1+}$ state. When a neutral oxygen atom is introduced it will be situated in the chain layer and ionize its two neighbouring copper atoms into the Cu$^{2+}$ state. If a second atom enters the layer at a position away from the other oxygen atoms, it will also ionize its two neighbouring copper atoms. However, if an oxygen atom enters the site next to another oxygen atom, it cannot further ionize the copper atom that lies between them, but must pull an electron in from elsewhere in the sample i.e: the CuO$_2$ plane. This leaves a hole in the CuO$_2$ plane. As the chains of oxygen atoms grow in length, the hole doping level in the planes increases. In reality, the situation is more complicated than this, with there being a minimum chain length greater than two required before electrons are pulled out of the planes [102].

### 6.2 Sample preparation

Extremely pure single crystals of YBa$_2$Cu$_3$O$_{6+x}$, with cation disorder at the $10^{-4}$ level, were grown in barium zirconate crucibles by Ruixing Liang at the University of British Columbia [99]. One of these crystals, with a thickness of 0.3 mm, was cut and polished with Al$_2$O$_3$ abrasive into a shape that I will refer to as an ellipsoid. The shape of the sample actually is roughly spherical, with no sharp edges or corners and two flat parallel surfaces remaining as remnants of the original $ab$-plane faces of the crystal. This sample shape was chosen as it has a smaller demagnetizing factor than a platelet and a smaller field enhancement at the equator than a platelet would have around its edges. Also, when attempting to induce pure $ab$-plane currents in a platelet there is a tendency for the current to short circuit the corners by travelling for a short distance along the $c$ axis. This mixes
the c-axis response in with the ab-plane response. In an ellipsoid, there are no corners for this to happen at. The mass of the sample was determined using a microgram balance, and this was used to compute an average radius of $183\pm5\,\mu m$. The oxygen content of the ellipsoid was adjusted to $O_{\theta.333}$ by annealing at $914^\circ C$ in flowing oxygen, followed by a homogenization anneal in a sealed quartz ampoule at $570^\circ C$ and a quench to $0^\circ C$. At this point the sample was not superconducting, but after a few weeks of room temperature,
ambient pressure annealing, $T_c$ rose to 3 K. A further increase in $T_c$ was achieved through high pressure annealing at room temperature.

The ellipsoid has now undergone five separate high pressure anneals at various pressures. The first four anneals all produced a $T_c$ of about 17 K, while the latest anneal, which was twice as long as any previous anneal, pushed the $T_c$ up to 20 K. As long as the sample is kept below about -10°C at ambient pressure, the dopant oxygen atoms are immobile, holding $T_c$ constant. Warming above 0°C results in oxygen disordering and rapidly reduces $T_c$.

Sample mounting was carried out in a refrigerated glove box at temperatures less than -5°C, and the sample is stored below -10°C when it is not being studied. In the main round of experiments I mounted the sample on one of its flat surfaces in the microwave magnetic field probe as shown in Figure 6.5. The surface impedance was measured at three dopings before the sample was sent back to the University of British Columbia. Jake Bobowski there performed bolometric measurements of the broadband microwave conductivity. The
sample was then returned to Simon Fraser University and remounted as before. I took measurements at 35 different dopings as $T_c$ was slowly relaxed back to 3 K using room temperature annealing. Throughout this doping sweep the sample remained in place in the microwave magnetic field probe. Following this, the sample and sample holder were removed from the microwave magnetic field probe and Laue diffraction was used to quantify the small misalignment of the sample with respect to the microwave magnetic field (for more information see Appendix B).

I then mounted the sample in our dilution refrigerator and measured the surface impedance over the temperature range 50 mK to 5 K. For these measurements the sample was not mounted on one of its flat surfaces, and thus there was a large misalignment between the sample’s $c$-axis and the microwave magnetic field. Following this the sample was sent back to the University of British Columbia for another high pressure anneal, after which it was mounted in the microwave magnetic field probe with its crystalline $c$-axis perpendicular to the microwave magnetic field so as to induce currents to flow along the $c$-axis. This $c$-axis data was then used to apply a small correction to the $ab$-plane data as detailed in Appendix B.
Chapter 7

Currents flowing in the \( ab \)-plane

Here I present results for currents flowing within the \( ab \) plane. The ellipsoid was mounted in the microwave magnetic field probe as described in Section 6.2 and measurements of the complex surface impedance were performed at 2.64 GHz. This was done using the \( \text{TE}_{011} \) mode of the resonator to induce current to flow predominantly within the \( ab \) plane. The ellipsoid initially had a doping with \( T_c = 17.5 \) K and measurements were performed at 38 separate dopings as \( T_c \) was slowly relaxed back down below 3 K via room temperature annealing. In this chapter I will first present the surface impedance data and the conductivity as determined from this data. This will be followed by an in-depth look at the low-energy excitation spectrum as determined by my measurements and a discussion of the scattering rate as determined by a two-fluid analysis of our data.

7.1 Surface impedance

Systematic measurements of the doping and temperature dependence of the complex surface impedance of the previously described \( \text{YBa}_2\text{Cu}_3\text{O}_{6.333} \) ellipsoid were performed using the cavity perturbation apparatus described in Chapter 5. The doping was varied over a \( T_c \) range of 3-18 K using the combination of high-pressure and room temperature annealing described in Chapter 6. A small misalignment between the sample’s crystalline \( c \) axis and the microwave magnetic field resulted in a contribution from the \( c \) axis in the raw data. This contribution enters as \( \sin^2 \theta Z_c \), where \( \theta \) is the angle between the crystalline \( c \) axis and the microwave magnetic field and \( Z_c \) the \( c \)-axis surface impedance. This was removed using the
procedure described in Appendix B. The low temperature portion of the resulting surface impedance data is shown in Figure 7.1. The thermal transition into the superconducting state in lead is sharp and shows no rounding to within the resolution limits of our measurements [1]. However, as shown in Figure 7.1, the transition is very broad in YBa$_2$Cu$_3$O$_{6.333}$. The broadening seen here is not due to inhomogeneity of $T_c$ throughout the sample, but rather due to an extraordinary amount of superconducting fluctuations above $T_c$, as will be discussed in detail in Section 8.2. Equation 2.35 implies that $\lambda(T) \propto X_s(T)$ in the superconducting state. If we look at the data in light this, then it would appear as though the penetration depth is not linear in temperature at low temperatures. However, in the next section we will find that this is not the case, since $1/\lambda(T)$ is proportional to $1 - AT$ and therefore $\lambda(T)$ grows linearly in temperature.

A kinetic inductance peak [103] can clearly be seen in $X_s$ at higher dopings, just below
$T_c$. This peak results from the inertial response of the current carriers as follows. In the normal state the conductivity is predominantly real. This leads to $R_s \approx X_s \approx \omega \mu_0 \delta/2$ where $\delta \equiv \sqrt{1/2\omega \mu_0 \sigma}$ is the real part of the skin depth. This contribution to the inductance is purely geometrical, i.e. it arises from the energy stored by the magnetic fields inside the sample. As temperature goes to zero, the conductivity becomes imaginary and large. This leads to $R_s \approx 0$ and $X_s \approx \omega \mu_0 \lambda$. In this limit the surface reactance not only has a geometric part ($= \omega \mu_0 \lambda/2$) but includes a kinetic part of equal magnitude, due to the energy stored in the accelerated superfluid. At low temperatures the penetration depth $\lambda$ is always shorter than the normal state skin depth $\delta$, which leads to an overall decreasing trend in $X_s(T)$ with decreasing temperature. The onset of the kinetic inductance on entering the superconducting state is an interesting process. It is driven by the first appearance of a nonzero imaginary part of the conductivity, $\sigma_2$, at $T_c$, which grows continuously on cooling. The imaginary part of the conductivity, which is proportional to the superfluid density $n_s$, has two effects on the reactance: first, it gradually increases the overall magnitude of the conductivity, $\sqrt{\sigma_1^2 + \sigma_2^2}$, which starts to shrink the length scale for field penetration. Secondly, and more abruptly, it rotates the phase angle of the conductivity, generating the kinetic contribution to inductance. The latter effect is first order in $\sigma_2$, while the prior is second order. For a small range of temperatures just below $T_c$, the increase in kinetic inductance outruns the decrease in geometric inductance, and a small peak in $X_s(T)$ is observed.

## 7.2 Conductivity

The local limit expression for the conductivity, Equation 2.32, is used to determine the conductivity $\sigma$ from the surface impedance $Z_s$. The superfluid density will be discussed first, then the real part of the conductivity. This will be followed by an examination of the broadband conductivity as measured by Jake Bobowski at the University of British Columbia.

### 7.2.1 Superfluid density

The imaginary part of the conductivity $\sigma_2 = 1/\omega \mu_0 \lambda^2(T)$ is plotted in Figure 7.2 as $1/\lambda^2$. Interestingly, after performing the full analysis, the superfluid density is seen to be linear
Figure 7.2: $ab$-plane superfluid density $\rho_{ab}$ plotted as $1/\lambda^2$. The top data set (orange) is at the highest doping ($T_c = 17.5$ K) while the bottom data set (green) is at the lowest doping ($T_c \approx 3$ K). The superfluid density is remarkably linear over a large range of both temperature and doping and crosses over to weaker temperature dependence at low temperatures.

in temperature from near $T_c$ down to about 5 K as is expected of a $d$-wave superconductor. Below 4 K there is a cross-over to an accurately quadratic temperature dependence. This is clearly shown by plotting $1/\lambda^2$ versus $T^2$ as in Figure 7.3a. In addition, with the sample at the lowest doping (in the fully relaxed state with $T_c \approx 3$ K) the sample was remounted in a microwave cavity in a dilution refrigerator and measured down to $T = 0.05$ K. This data is plotted versus $T^2$ in Figure 7.3b. The quadratic behaviour is seen to be robust down to the lowest temperatures, neither flattening out to activated exponential behaviour nor turning
up to reveal a power law intermediate between \( T^1 \) and \( T^2 \). At higher temperatures the data peals away from \( T^2 \) due to the proximity of \( T_c \). It will be shown later in this chapter that this temperature dependence is consistent with \( d \)-wave superconductivity in the presence of a small density of pair-breaking defects, as is well established in \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) at higher dopings [52, 104, 105].

A useful characterization of the strength of pair-breaking is provided by the temperature \( T_d \) at which \( \rho_s(T) \) crosses over from quadratic to linear behaviour. Using an interpolation formula, \( \Delta \rho_s(T) = AT^2/(T + 2T_d) \), similar to that of Ref. [105], \( T_d \) is defined to be the point at which the slope of the high temperature linear behaviour, \( \Delta \rho_s = \alpha T \), matches the slope of the low temperature quadratic behaviour, \( \Delta \rho_s = \beta T^2 \). Using values of \( \alpha \) and \( \beta \) obtained from fits similar to those shown in Figure 7.3 and Figure 7.4a, we plot \( T_d \equiv \alpha/2\beta \) in Figure 7.4b. The crossover temperature lies between 4 K and 5 K at these low dopings and shows very little doping dependance. This cross-over temperature is larger than in the

Figure 7.3: (a) Low temperature limit of the superfluid density plotted versus \( T^2 \) to show the low temperature power law. (b) Data taken down to 50 mK in our dilution refrigerator and plotted versus \( T^2 \). The line demonstrates that the low temperature behaviour is \( T^2 \). The higher temperatures the data peals away from \( T^2 \) due to the proximity of \( T_c \).
best samples of Ortho-II YBa$_2$Cu$_3$O$_{6.50}$ and Ortho-I YBa$_2$Cu$_3$O$_{6.99}$, where $T_d$ is less than 1 K. This may be linked to the lower degree of CuO chain order in YBa$_2$Cu$_3$O$_{6.333}$, which is known to be an important source of residual scattering in the best YBa$_2$Cu$_3$O$_{6+x}$ samples [106], but $T_d$ is also likely to be enhanced by proximity to the Mott insulating state. $T_d$ is expected to be closely linked to the single-particle scattering rate, $1/\tau_{sp}$. In the strong scattering limit, discussed in Ref. [105], $T_d = 0.33h/k_B\tau_{sp}$, from which we would infer $h/k_B\tau_{sp} \approx 13.5$ K from our data. At first sight, there seems to be a large discrepancy with respect to the relaxation rate obtained from $\sigma_1(\omega)$. However, the rate at which electrical currents relax is always smaller than the single particle scattering rate, as more than one
scattering event is usually required to fully randomize momentum. The difference between the two scattering rates can be particularly strong in a $d$-wave superconductor [60], especially in situations where small-angle scattering is important, such as from out-of-plane defects. Also shown in Figure 7.4b is the residual DOS, expressed in superfluid density units as $\Delta \rho_s$, inferred from the difference between linear and quadratic extrapolations of $\rho_s(T)$ to $T = 0$. $\Delta \rho_s$ falls on underdoping, but remains a roughly constant fraction of $\rho_s(T = 0)$, consistent with the weak doping dependence of $T_d$.

### 7.2.2 Real part of the conductivity

The real part of the conductivity $\sigma_1$ as determined from Equation 2.32 is shown in Figure 7.5. A fluctuation peak, associated with thermally-induced short-lived Cooper pairs, occurs near $T_c$ for all dopings. The fluctuation conductivity will be discussed in more detail in Section 8.2. If the fluctuation peak is ignored, then the conductivity appears to increase in the superconducting state. This indicates a decrease in the scattering rate upon entering the superconducting state as will be shown in Section 7.4. At the lowest temperatures and
CHAPTER 7. CURRENTS FLOWING IN THE AB-PLANE

at the highest dopings the conductivity then appears to decrease slightly as the temperature is lowered as would be expected as the normal carriers condense into the superfluid. This behaviour does not appear similar to what is seen in optimally doped YBa$_2$Cu$_3$O$_{6+x}$, but is very similar to what is seen in optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [107]. Nunner and Hirschfeld [107] have provided a compelling explanation for the difference between the conductivities of these two materials, namely, that Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ contains a large concentration of weak extended scatterers, attributed to out-of-plane disorder introduced by doping, while optimally doped YBa$_2$Cu$_3$O$_{6+x}$ has very little out-of-plane disorder due to low cation disorder and its proximity to one of the “special” oxygen contents discussed in Chapter 6. The difference between our sample, and optimally doped YBa$_2$Cu$_3$O$_{6+x}$ is related to the oxygen content and ordering in the chain layers. This extra disorder likely provides the weak extended scattering necessary to produce a conductivity similar to that of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$.

In theories of critical fluctuations in superconductors the fluctuation peak at $T_c$ should be cusp-like, with infinite slope at $T_c$ [108]. However, any disorder or distribution of transition temperatures will cause broadening of the fluctuation peak [109]. Knowing this, we use the temperature difference between the points of inflection on either side of the peak as a measure of $\Delta T_c$ as will be discussed further in Section 8.1.2.

7.2.3 Broadband conductivity

Broadband spectroscopy of the quasiparticle conductivity $\sigma_1(\omega, T)$ has been carried out by Jake Bobowski at UBC using bolometric measurements of $R_s(\omega, T)$ between 0.1 and 20 GHz, as described in Refs. [53] and [110]. The YBa$_2$Cu$_3$O$_{6.333}$ ellipsoid and a Ag:Au reference sample were positioned in symmetric locations at the end of a rectangular coaxial transmission line, with the microwave $H$-field oriented along the $c$ axis of the ellipsoid. $R_s(\omega, T)$ has been inferred from the synchronous rise in sample temperature in response to incident microwave fields modulated at 1 Hz. The Ag:Au sample acts a power meter, providing an absolute calibration. At low frequencies, $\sigma_1$ can be obtained from $R_s$ and knowledge of the penetration depth: in this limit $\sigma_1 \approx 2R_s/\omega^2\mu_0^2\lambda^3$. At higher frequencies, the quasiparticle conductivity starts to contribute to electromagnetic screening, effectively reducing $\lambda$. The shielding effect of the quasiparticle currents must be taken into account
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Figure 7.6: (a) Broadband bolometric measurement of the surface resistance, $R_s(\omega)$, at $T = 1.7$ K. Data are for a doping state with $T_c = 15.6$ K. The solid line is a fit using the phenomenological conductivity model, Equation 2.24, with $y = 1.7$. A fit with $y = 1.4$ is practically indistinguishable and provides an equally good representation of the data. The dashed line, a best fit to the Drude model ($y = 2$), shows clear deviations at high frequencies. (b) The real part of the conductivity spectrum determined from the $R_s(\omega)$ data in (a). The solid line is a fit to the conductivity spectrum for $y = 1.7$ using the phenomenological model Equation 2.24. The small, narrow peak at low frequencies is a robust result of the analysis but is of uncertain origin.

self-consistently, and the procedure for doing this is described in detail in Appendix C of Ref. [110]. As part of this process, the quasiparticle contribution to $\sigma_2$ is inferred from a Kramers–Krönig transform of $\sigma_1(\omega)$. This in turn requires a robust means of extrapolating $\sigma_1(\omega)$ outside the measured frequency range. Here we use Equation 2.24 with $y = 1.4$ and $y = 1.7$ which spans the range of exponents used in previous analyses of the quasiparticle conductivity in YBa$_2$Cu$_3$O$_{6+x}$ [53, 111]. Both $y$ values provide equally good fits to the data, as seen in Figure 7.6a. It can also be seen that a Drude fit ($y = 2$) deviates from the data at high frequency. Figure 7.6b shows the real part of the conductivity spectrum determined from the $R_s(\omega)$ data in Figure 7.6a. The solid line is a fit to the conductivity spectrum for
CHAPTER 7. CURRENTS FLOWING IN THE AB-PLANE

$y = 1.7$ using Equation 2.24. At low frequency there is a narrow peak in $\sigma_1(\omega)$, of uncertain origin, which may indicate long lived currents, possibly associated with superconducting fluctuations. In any case it represents an insignificant fraction of the total oscillator strength, and is therefore omitted from the fitting procedure by using a weighting function that fits preferentially to the higher frequency data. From the fits the uncondensed spectral weight can be calculated for different choices of exponent $y$. Expressed in superfluid density units, we obtain $\Delta \rho_s = 1.05 \mu m^{-2}$ for $y = 1.4$ and $\Delta \rho_s = 0.70 \mu m^{-2}$ for $y = 1.7$. Additionally, the fits to $\sigma_1(\omega)$ also provide a measure of the average relaxation rate of electrical transport currents, $1/\tau_{tr}$, from the width parameter $1/\tau$. For $y = 1.4$ and 1.7, respectively, we find that $1/\tau_{tr} = 24$ GHz and 26 GHz, or about 1.2 K in temperature units. This will later be compared to the values of the scattering rate inferred from pair-breaking effects.

Although it would be useful to study the doping dependence of $1/\tau_{tr}$, at this point the broadband microwave spectroscopy experiments have only been carried out at one doping. It is difficult to obtain information about the residual scattering rate by other means, such as extrapolation of the normal-state resistivity as, in that case the presence of strong superconducting fluctuations and a $\ln(T)$ upturn make the extrapolation to zero temperature unreliable.

### 7.3 Competing and coexisting orders

As a sensitive thermodynamic probe that couples directly to current-carrying excitations, measurements of superfluid density are well suited to detecting changes in the nodal quasiparticle spectrum arising from competing orders and other physics. When we add to this information extracted from measurements of the broadband conductivity, which probes the spectral weight of the zero-energy quasiparticles, we are able to place strong limitations on the types and strengths of any competing orders in highly underdoped YBa$_2$Cu$_3$O$_{6+x}$.

#### 7.3.1 Theory

A number of authors have investigated theoretically the effects of orders that compete or coexist with pure $d_{x^2-y^2}$ superconductivity. Sharapov and Carbotte [112] have performed calculations of $\rho_s$ in the low temperature limit for a $d_{x^2-y^2} + id_{xy}$ order parameter and for
incommensurate spin density waves that nest the nodal points (nested SDW), obtaining analytic results for $\rho_s(T \to 0)$ and its leading temperature corrections. In the absence of disorder they find that both the nested SDW and the $d_{x^2-y^2} + id_{xy}$ superconductor have a finite gap everywhere on the Fermi surface, leading to activated exponential behaviour $\rho_s(T) \sim \exp(-\Delta' / k_B T)$, where $\Delta'$ is the magnitude of the SDW or $d_{xy}$ gap. However, nested SDW orders compete for Fermi surface, removing nodal states from the $T = 0$ condensate. In contrast, a transition to a clean $d_{x^2-y^2} + id_{xy}$ state leaves $\rho_s(T \to 0)$ unchanged. Unfortunately, this distinction is difficult to detect experimentally because $\lambda_0$ is neither known a priori nor can the absolute value of $\lambda(T \to 0)$ usually be measure with sufficient accuracy. In the presence of disorder, both the nested SDW and $d_{x^2-y^2} + id_{xy}$ states develop a leading quadratic temperature dependence, $\rho_s \sim T^2$, similar to that of a dirty $d_{x^2-y^2}$ superconductor. However, an experimentally detectable difference now arises: pair-breaking in the $d_{x^2-y^2} + id_{xy}$ state is accompanied by zero-energy quasiparticles, whereas the disordered SDW continues to remove low energy states without creating a residual DOS. Atkinson has studied the competition between nested, incommensurate SDW and $d_{x^2-y^2}$ superconductivity numerically and finds broadly similar results [113], pointing out that on the basis of the temperature dependence of $\rho_s$ alone, the effect of disordered magnetism cannot be distinguished from dirty but pure $d$-wave superconductivity. He shows that the suppression of zero-temperature superfluid density in the nested SDW case arises because nodal Cooper pairs cease to carry a well-defined current. Modre et al. [114] have studied the $d_{x^2-y^2} + is$ pairing state, which also has a finite energy gap and activated behaviour in $\rho_s(T)$ at low temperature. In contrast to the $d_{x^2-y^2} + id_{xy}$ case, the $d_{x^2-y^2} + is$ gap is stable in the presence of disorder of any strength. In Appendix C we show from an experimentalist’s perspective how this arises from impurity renormalization of the $s$-wave gap component.

The stability of the nodal quasiparticle spectrum in the presence of commensurate competing orders of all types has been studied by Berg et al. [116]. For commensurate perturbations that do not nest the nodal points, they prove that if the perturbation is invariant under time reversal or time reversal followed by a lattice translation, the nodal spectrum is stable. One example of this is competition from nematic order, which has been shown to shift the nodes in $k$-space, but leave the nodal structure intact [117]. While it remains uncertain whether the converse of their result holds in general, Berg et al. have examined several important cases in which the nodal spectrum breaks down, including certain stripe-like ar-
CHAPTER 7. CURRENTS FLOWING IN THE AB-PLANE

Figure 7.7: (a) The presence of a perturbation of the form given by Equation 7.1, from the $\Theta_{II}$-type circulating currents shown in Figure 7.7b, modifies the nodal spectrum of the $d_{x^2-y^2}$ superconductor in a characteristic way: one node is shifted up in energy by $\approx 4\Delta_{cc}$, one is shifted down, and two are unperturbed. (b) Individual nodal contributions to the density of states $N(\omega)$ from a circulating current perturbation of the form given by Equation 7.1. Inset, upper left: the $\Theta_{II}$ circulating current pattern proposed in Ref. [115]. Inset, lower right: an equivalent current pattern within a one-band model of the CuO$_2$ planes [116].

$.\,$

The arrangements of spin and charge density, and the $\Theta_{II}$ circulating-current phase that has been detected by neutron scattering in YBa$_2$Cu$_3$O$_{6+x}$ and HgBa$_2$CuO$_{4+\delta}$. Confining themselves to a one-band model of the CuO$_2$ planes, Berg et al. have used the simpler arrangement of orbital currents shown in Figure 7.7b, which is equivalent to the $\Theta_{II}$ state in the more complicated three-band Cu–O lattice of Ref. [115]. For a perturbation to the pure $d_{x^2-y^2}$ superconductor of the form

$$W = -i\Delta_{cc} \left\{ \sum_{rr'\sigma} \eta_{rr'} c_{r\sigma}^\dagger c_{r'\sigma} + \text{h.c.} \right\}, \quad (7.1)$$

where $\eta_{rr'} = \pm 1$ is determined by the direction of the bond currents in Figure 7.7b, they find excitation energies $E_k^\pm = E_k^0 + 2\Delta_{cc} \{\sin(k_xa) - \sin(k_ya) + \sin[(k_y - k_x)a]\}$. Here
\( E^0_k \) is the unperturbed \( d \)-wave spectrum and \( \alpha \) is the lattice spacing. The perturbed nodal spectrum for the \( \Theta_{II} \) state is plotted in Figure 7.7a. The effect of the circulating currents is similar to the Doppler shift from a uniform current applied along a diagonal direction: one node shifts up in energy by \( \approx 4\Delta_{cc} \), one node shifts down, and two are unperturbed. The individual contributions to the low energy DOS are plotted in Figure 7.7b and the combined DOS is shown in Table 7.1. The net effect on \( N(\omega) \) is a finite residual DOS \( \approx 2\Delta_{cc}/\Delta_0 \), and a kink at \( \omega \approx 4\Delta_{cc} \) above which the linear energy dependence doubles in slope. In the clean limit, the superfluid density can be obtained from Equation 2.36 or Equation 2.37 and is plotted in Table 7.1. The limiting low temperature behaviour of \( \rho_s(T) \) is linear, arising from excitations near the two unperturbed nodes. At a temperature of order \( 4\Delta_{cc}/k_B \), \( \rho_s(T) \) crosses over to a second linear regime in which all four nodes contribute and the temperature slope doubles. In a clean sample, the combination of a residual DOS and a kink in \( \rho_s(T) \) separating two linear regimes should be easily observable in experiments. Calculations in the presence of disorder have not been carried out, but we expect strong scattering impurities to induce additional residual DOS and to cause a crossover to \( T^2 \) behaviour in \( \rho_s(T) \), as is seen in \( d_{x^2-y^2} \) and \( d_{x^2-y^2} + id_{xy} \) superconductors. Although disorder will mask the effect of circulating currents when the crossover temperature \( T_d \geq 4\Delta_{cc}/k_B \), it is expected that tight limits on the size of \( \Delta_{cc} \) can nevertheless be placed, either using \( \rho_s(T) \) or from the magnitude of the uncondensed spectral weight in \( \sigma_1(\omega,T \to 0) \).

The effect of competing orders on \( \rho_s(T) \) and the residual DOS is summarized in Table 7.1. The SDW results are for the case of ordering wavevectors that nest the nodal points. The response to nested charge density waves is expected to be broadly similar, with the opening of a finite nodal gap that competes for Fermi surface.

### 7.3.2 Limits on competing orders

We are able to draw tight conclusions from our measurements of the superfluid density and broadband conductivity about the types and magnitudes of electronic order than might be competing with pure \( d_{x^2-y^2} \) superconductivity in \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \). We emphasize that to do this it is essential to have measurements of both the asymptotic low temperature form of \( \rho_s(T) \), and the residual DOS from \( \sigma_1(\omega) \). On the basis of the limiting quadratic \( T \) dependence, which we have followed down to 0.05 K, we can rule out any of the clean-
limit behaviours shown in Table 7.1, as well as the $d_{x2-y2} + is$ state in the presence of disorder. We can also exclude the BCS–BEC crossover scenario, which predicts a $T^{3/2}$ term in $\rho_s(T)$ from incoherent Cooper pairs excited from the condensate. When disorder is included, four of the remaining states in Table 7.1 are compatible with quadratic behaviour in $\rho_s(T)$. Of these, nested spin and charge density waves can immediately be eliminated, as they are not expected to be accompanied by a residual DOS. Of the remaining three, the simplest possibility is pure $d_{x2-y2}$ superconductivity in the presence of a small amount of strong scattering disorder. However, we cannot rule out a small $id_{xy}$ component, nor a weak $\Theta_{II}$-type circulating current phase. Nevertheless, we can place tight limits on the size of such effects. We show in Figure C.1 that the $id_{xy}$ state only becomes visible once $\Delta_{d_{xy}} > k_B T_d$. Similarly, we would expect the clean-limit behaviour of the $\Theta_{II}$ state to be apparent once $4\Delta_{cc} > k_B T_d$, meaning that if a perturbation of the form given by Equation 7.1 is present, then $\Delta_{cc}$ must be 2.4 K or less.\(^{1}\) The constraints become even tighter in Ortho-II \(\text{YBa}_2\text{Cu}_3\text{O}_{6.50}\) and Ortho-I \(\text{YBa}_2\text{Cu}_3\text{O}_{6.99}\), where the disorder scale $T_d$ is less than 1 K.

\(^{1}\)Although the effect of disorder on $\rho_s$ in the $\Theta_{II}$ state has not been calculated, a rigorous upper bound is set by the residual density of states, which is observed to be about 15% from broadband quasiparticle spectroscopy of $T_c = 15.6$ K material. Conservatively assigning all of this to circulating current effects, we would have $\Delta \rho_s / \rho_s(T = 0) = 0.15 \approx 2\Delta_{cc} / \Delta_0 \approx \Delta_{cc} / k_B T_c$, implying $\Delta_{cc} / k_B \lesssim 2.4$ K.

Table 7.1 (following page): Effect of competing orders on the superfluid density of a $d_{x2-y2}$ superconductor. The first column shows results for the pure $d_{x2-y2}$ state. Subsequent columns show the effect of competition from: $\Theta_{II}$-type circulating currents Varma [115], Berg et al. [116]; $d_{x2-y2} + is$ superconductivity [114]; $d_{x2-y2} + id_{xy}$ superconductivity [112]; and spin density waves (SDW) that nest the nodal points [112, 113]. The first row shows clean-limit excitation spectra for the near-nodal quasiparticles. The second row gives the density of states (DOS) $N(\omega)$, both for clean systems and in the presence of disorder. Note that the effect of disorder has not been calculated for the $\Theta_{II}$-type perturbation, and that nonmagnetic disorder has essentially no effect on the $d_{x2-y2} + is$ superconductor. The third row shows the temperature dependence of the superfluid density $\rho_s(T)$, including deviations from full condensation as $T \to 0$ due to the presence of zero-energy quasiparticles. The fourth row indicates whether a residual density of states is expected to be seen in $\sigma_1(\omega, T \to 0)$, and the fifth row gives the leading low temperature behaviour of the superfluid density. Details of the calculations are given in Appendix C for the $d_{x2-y2}$, $d_{x2-y2} + is$ and $d_{x2-y2} + id_{xy}$ states. Dirty limit calculations have been made for unitarity limit scatterers.
### CHAPTER 7. CURRENTS FLOWING IN THE AB-PLANE

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<th>$d_{x^2-y^2}$</th>
<th>$\Theta_{II}$ current loops</th>
<th>$d_{x^2-y^2} + i$</th>
<th>$d_{x^2-y^2} + id_{xy}$</th>
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#### Energy spectrum

- $E(k)$
- $k_\perp$
- $k_x$

#### DOS

- **Clean** – solid
- **Dirty** – dashed

#### $\rho_s(T)$

- **Clean** – solid
- **Dirty** – dashed

<table>
<thead>
<tr>
<th>residual</th>
<th>clean</th>
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<th>clean</th>
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<tr>
<td>DOS</td>
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<td>$e^{-\Delta_s/k_BT}$</td>
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<td>$Te^{-\Delta_{SDW}/k_BT}$</td>
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<tr>
<td>$\Delta \rho_s(T)$</td>
<td>$T$</td>
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<td>$e^{-\Delta_{xy}/k_BT}$</td>
<td>$Te^{-\Delta_{SDW}/k_BT}$</td>
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Finally, while we can rule out nested spin and charge density waves, our data say very little about commensurate orders that connect parts of the Fermi surface away from the nodes, as these will generally not alter the low energy spectrum. One such a scenario has been revealed by recent STM measurements on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [28], which show ordered, nondispersing modulations of the DOS at high energies and simultaneously, at low energies, arcs of Bogoliubov quasiparticles associated with the nodal $d_{x^2-y^2}$ spectrum. The ‘Bogoliubov arcs’ appear to terminate on the Bragg plane joining $(0, \pi)$ and $(\pi, 0)$ points, leaving the nodal spectrum intact. This would be compatible with the conclusions we draw here about YBa$_2$Cu$_3$O$_{6+x}$.

### 7.4 Two-fluid analysis

We have measured both the real and imaginary parts of the conductivity and, as a result, we can perform a two-fluid analysis of the data. For computational ease a Drude line-shape is assumed for the frequency dependence of the conductivity. Near $T_c$ this will fail to accurately describe the conductivity as there will be an extra contribution to the conductivity due to the fluctuations. However, well below $T_c$ a single component spectrum should give an accurate account of the electrodynamic response. The scattering rate $1/\tau$ has been obtained using Equation 2.28 and is plotted versus temperature in Figure 7.8a. The normal fluid fraction, determined via Equation 2.29, is shown in Figure 7.8b. The failure of a single component spectrum to capture the fluctuation physics near $T_c$ leads to the apparent dip in $1/\tau$ near $T_c$. This is an artefact of the analysis, and does not reflect actual changes in the scattering rate. Below the dip, particularly at the higher dopings (see the inset of Figure 7.8a), the scattering rate has a linear temperature dependence before it flattens to a constant value at the lowest temperatures. At the lowest temperatures $1/\tau$ ranges from 2 to $5 \times 10^{11}$ s$^{-1}$. Using a Fermi velocity $v_F = 2.6 \times 10^5$ m/s, which seems to be a universal value for all dopings and cuprate materials [73], results in mean free paths varying from 0.5 to 1.3 $\mu$m. This scattering rate is slightly larger than that which is implied by the broadband conductivity measurements discussed in Section 7.2.3; the latter gave a scattering rate of 25 GHz or $1.6 \times 10^{11}$ s$^{-1}$. This discrepancy is likely due to the assumption of a Drude spectrum in our two-fluid analysis. Özcen et al. [111] have shown that the use of a more realistic spectral shape results in a scattering rate that is approximately 1.5 times smaller.
Figure 7.8: (a) The scattering rate as determined from Equation 2.28. The dip near $T_c$ is due to fluctuations and does not reflect the true value of the scattering rate. At the lowest temperatures the scattering rate varies from 2 to $5 \times 10^{11}$ s$^{-1}$ which corresponds to a mean free path of 0.5 to 1.3 $\mu$m. Inset: The scattering rate at 5 dopings ($T_c$’s between 11.8 and 13 K). Below the dip the scattering rate appears to be linear in temperature before flattening out to a constant value at the lowest temperatures. (b) The normal fluid fraction determined via Equation 2.29. From this analysis it appears as though the uncondensed fraction at zero temperature increases with underdoping.

than when a Drude spectrum is used.

A simple application of the two-fluid analysis above $T_c$ leads to two unphysical results: a temperature independent scattering rate; and a very strong doping dependence of $1/\tau$. As we will explain in Chapter 10, these discrepancies can be resolved by recognizing that the sample is likely entering the dirty limit and, in fact, an extension of the analysis then provides important information on the magnitude of the superconducting gap.

The normal fluid fraction as determined by Equation 2.29 is shown in Figure 7.8b. Since $\omega \tau$ is small the normal fluid fraction tracks the linear temperature dependence of the superfluid density. We can also see that the uncondensed fraction appears to increase with underdoping. While it would be useful to confirm this using broadband techniques, this
has not been done at this time, as the broadband measurements are very difficult and time consuming.
Chapter 8

The effects of fluctuations

This chapter will discuss the effects of fluctuations on the $ab$-plane data. We start with the superfluid density and discuss the surprising lack of a Kosterlitz-Thouless transition or 3D-XY critical behaviour. This leads into a discussion of the effects of quantum criticality on the magnitude of the zero-temperature superfluid density. We then focus on the temperature and magnetic field dependence of the resistive transition into the superconducting state.

8.1 Superfluid density

One of the most striking features of the temperature dependence of the superfluid density, as shown in Figure 8.1, is the nature of the transition into the superconducting state. The transitions, at least within the limits imposed by inhomogeneity, appear mean-field-like, with no sign of critical fluctuations or vortex unbinding. At optimal doping, YBa$_2$Cu$_3$O$_{6+x}$ is the most three-dimensional cuprate superconductor, with $\lambda^2_c(T \to 0)/\lambda^2_{ab}(T \to 0) \approx 50$ [118]. Its critical behaviour at optimal doping has been firmly established to be in the 3D-XY universality class [83–85], with the superfluid density going to zero at $T_c$ like $1/\lambda^2 \propto (1 - T/T_c)^{0.66}$. However, at these low dopings we see $1/\lambda^2 \propto (1 - T/T_c)$. The major difference here is that in the highly underdoped regime $\lambda^2_c(T \to 0)/\lambda^2_{ab}(T \to 0) \approx 10000$ as $1/\lambda^2_c(T \to 0) = 50 - 700 \text{ mm}^{-2}$ and $1/\lambda^2_{ab}(T \to 0) = 0.5 - 7 \mu\text{m}^{-2}$. Under these circumstances, one would at first sight anticipate fluctuations in adjacent layers to be uncorrelated. This would then result in a Kosterlitz-Thouless-Berezinsky (KTB) vortex-unbinding transition [57, 79] occurring as described in Section 4.1. The dashed and solid
Figure 8.1: The \( ab\)-plane superfluid density \( \rho_{ab}^{\ast} \) plotted as \( 1/\lambda^2 \). The superfluid density is remarkably linear over a large range of both temperature and doping and crosses over to weaker temperature dependence at low temperatures. The two lines mark where the vortex-unbinding transition should occur for a 2D superconductor, with the dashed line corresponding to individual CuO\(_2\) planes and the solid line corresponding to coupled CuO\(_2\) bilayers.

Lines in Figure 8.1 represent where the KTB transition would be expected to occur, for isolated CuO\(_2\) planes and bilayers, respectively. However, we do not see a collapse of the superfluid density at these lines. Instead \( \rho_s(T) \) passes smoothly through both lines, with no indication of vortex unbinding. This implies that fluctuations remain correlated over many unit cells in the \( c \) direction even though the anisotropy in this highly underdoped material is quite large. This is supported by recent work on YBa\(_2\)Cu\(_3\)O\(_{6+x}\) thin films, where KTB transitions are shown to occur, but the effective thickness for the fluctuations is the film thickness [86].
Figure 8.2: (a) My $\rho_{s0}(p)$ data (solid diamonds) and $T_c(p)$ from Ref. [119] (solid circles). Hole doping for the superfluid density is determined from our values of $T_c$, using a linear fit and extrapolation of the $T_c(p)$ data from Ref. [119] (solid line). If this extrapolation is valid, then $\rho_{s0}(p) \sim (p - p_c)^2$ at the onset of superconductivity, before crossing over to a linear doping dependence. The dashed line is a linear fit to $\rho_{s0}(p)$ at higher doping. (b) The result of assuming a linear mapping between doping and $\rho_{s0}$ (solid diamonds). $T_c$ (open squares) now varies as $(p - p_c)^{1/2}$ as $p \to p_c$. The solid line is a square-root $T_c(p)$ curve for comparison. $T_c(p)$ data from Ref. [119] (solid circles) are sparse in this range, and do not contradict our mapping. Vertical bars on the $T_c$ data show transition widths estimated from rounding of $\sigma_1(T)$ fluctuation peaks as described in Section 7.2.2. The corresponding spread in doping (horizontal bars) shows little variation with doping.

8.1.1 Quantum critical point

My measurements also reveal a strong correlation between $T_c$ and $\rho_{s0}$, with $\rho_{s0}$ falling continuously to zero on underdoping. However, contrary to the ultra-thin film studies, I find that $\rho_{s0}$ varies linearly with $T_c$ at higher doping and quadratically with $T_c$ at lower doping as shown in Figure 8.2a. The doping in Figure 8.2a has been determined from the data of Ref. [119]. In their recent experiments on the doping state of the CuO$_2$ planes in YBa$_2$Cu$_3$O$_{6+x}$, Liang et al. [119] have established a mapping between $T_c(x)$ and $p$, the hole concentration per planar Cu atom. A linear fit to the $T_c(p)$ data of Liang et al. [119] has
Figure 8.3: $\rho_{s0}(p)$ taken from our measurements and from the Gd ESR measurements of Ref. [118]. A linear extrapolation of our $\rho_{s0}(p)$ data (solid black line) passes within 5% of values of $\rho_{s0}$ from Ortho-II and fully-oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ extracted from Gd ESR measurements.

been used to determine $p$ and plot $\rho_{s0}(p)$. The linear doping dependence of $\rho_{s0}$ appears very robust: an extrapolation of the linear fit shown in Figure 8.2a passes within 5% of the $ab$-averaged superfluid density of both Ortho-II and fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [118] as shown in Figure 8.3. If the linear extrapolation of $T_c(p)$ to zero holds true then $\rho_{s0}(p)$ varies approximately quadratically with doping close to the onset of superconductivity. However, this is very hard to understand theoretically and an alternative proposal may be compelling.

While the lack of a KTB transition may not be surprising, the lack of a critical regime is since, at higher dopings, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ shows a large 3D-XY critical region [83–85]. Considering this, it is surprising that we see no critical regime near $T_c$ but instead see a mean-field transition. One would expect phase fluctuation effects to become more pronounced as the system is underdoped towards the Mott insulating state. However, the ob-
served behaviour is entirely consistent for a system approaching a quantum critical point (QCP) [81]; near the QCP the classical fluctuation region’s width is much reduced, and likely invisible to experiments.

If we are indeed near a QCP then the transition out of the superconducting state may be controlled by quantum critical fluctuations. In the scaling theory of a quantum phase transition, physical properties should be related to a single, divergent correlation length, $\xi \propto |x|^{-\nu}$, where $x = (p - p_c)$. Scaling analysis of the $XY$ model predicts $T_c \propto \xi^{-z} \propto |x|^{\nu z}$ and $\rho_{s0} \propto \xi^{-(d-2+z)} \propto |x|^\nu (d-2+z)$, where $z$ is the dynamical critical exponent [79, 120, 121]. Together, these relations imply $T_c \propto \rho_{s0}^{z/(d-2+z)}$, independent of $\nu$. In two dimensions ($d = 2$) this requires $T_c \propto \rho_{s0}$, whereas our measurements show $T_c \sim \rho_{s0}^{1/2}$. In three dimensions ($d = 3$), $T_c \propto \rho_{s0}^{z/(1+z)}$ and is consistent with our observations if $z = 1$, the so-called $(3+1)$D-$XY$ universality class [81]. The upper critical dimension of the $XY$ model is $D = 4$, so mean-field critical behaviour ($\nu = \frac{1}{2}$) should follow. However, this choice of $\nu$ is not compatible with the doping dependence of $T_c$ and $\rho_{s0}$ shown in Figure 8.2a: scaling arguments predict $T_c \propto x^{1/2}$ and $\rho_{s0} \propto x$, whereas the analysis shown in Figure 8.2a has $T_c \propto x$ and therefore $\rho_{s0} \propto x^2$. This difficulty may well stem from our determination of doping in Figure 8.2a, which is based on a linear fit and extrapolation of the $T_c(p)$ data from Liang et al. [119]. The sparseness of the $T_c(p)$ data, along with the lack of an anchor point as $T_c \to 0$, allows a different interpretation in the low doping regime. In Figure 8.2a, all data with $T_c \geq 8$ K follow an accurately linear doping dependence of the zero temperature superfluid density, which, as mentioned earlier, extrapolates to within 5% of much higher doped YBa$_2$Cu$_3$O$_{6+x}$ as shown in Figure 8.3. The robustness of this form leads us to put forward the following suggestion as a means of understanding the data. We propose that $\rho_{s0}(p)$ is, in actual fact, proportional to $(p - p_c)$ in the low doping range and use this linear mapping to determine $T_c(p)$. The results of this analysis are shown in Figure 8.2b. The mapping leaves $T_c(p)$ consistent with the data of Liang et al. [119]; the effect is simply to refine the $T_c(p)$ curve in the vicinity of the critical doping. $T_c(p)$ now grows initially as $(p - p_c)^{1/2}$, in accord with scaling arguments, before crossing over to a linear doping dependence at higher dopings. Over a substantial doping range this yields the well-known result that $T_c$ scales approximately with $\rho_{s0}$ [75].
Figure 8.4: The fluctuation peaks in the $ab$-plane conductivity are used to estimate the spread of $T_c$ within the sample. Theory predicts a cusp-like peak [108], so $\Delta T_c$ is defined as the temperature difference between the points of inflection above and below the peak. The peaks broaden as the doping is lowered, implying an increase in $T_c$ spread, however this does not imply an increase in doping spread, as shown in Section 8.1.2.

8.1.2 Transition widths

In addition, our proposed interpretation gives a plausible explanation of another aspect of the data. At the lowest dopings, the fluctuation peaks in $\sigma_1(T)$ broaden considerably, as shown in Figure 8.4 and the vertical bars in Figure 8.2b. In the presence of small, macroscopic variations in oxygen concentration, such broadening would be a natural consequence of a steepening of $T_c(p)$ on the approach to $p_c$. Future experiments, including those of the sort carried out by Liang et al. [119], will be needed to confirm our conjecture. However, the proposed scenario has several compelling features, not the least of which is a substantial simplification of our theoretical picture of the transition from non-superconductor to superconductor in the underdoped cuprates.

8.2 Resistivity and superconducting fluctuations

Since the normal state scattering rate is so large, as seen in the previous chapter, measurements at gigahertz frequencies are essentially equivalent to dc measurements except very close to $T_c$. This allows the normal state resistivity (one over the real part of the conductivity) to be analyzed using DC limit expressions.
Figure 8.5: (a) The $ab$-plane resistivity shown at 11 of 39 dopings measured in this study. At the lowest doping (uppermost trace) we see the familiar $\ln(1/T)$ upturn. As the doping is increased fluctuations hide the upturn and produce substantial rounding near $T_c$. The lines are fits to the data using Equation 8.1 and Equation 4.6 acting in parallel. (b) The temperature dependence of the $ab$-plane resistivity is nearly linear in temperature squared as can be seen by plotting $\rho_{ab}(T)$ versus $T^2$.

**8.2.1 Normal state resistivity**

In Figure 8.5a we show a subset of our measured datasets that span our doping range. The data is quantitatively and qualitatively similar to the data from dc resistivity measurements on samples with similar $T_c$ [122, 123]. At the lowest doping we have measured (with $T_c$ driven to 0), the well-known $\ln(1/T)$ upturn is clearly seen [124], while at higher dopings the fluctuation conductivity masks this feature. At higher temperatures the temperature dependence appears to be quadratic, as seen more clearly in Figure 8.5b and previously noted by Sun et al. [125]. These observations lead us to a phenomenological model of the normal state resistivity, namely:

$$\rho_{n}^{ab} = \rho_0 + AT^2 - c \ln T,$$  \hspace{1cm} (8.1)
Figure 8.6: (a) $ab$-plane magnetoresistivity data taken on the same sample by Xiaoqing Zhou and plotted versus temperature. Data were taken at fields of (from bottom to top): 0, 0.25, 0.5, 1, 3, 5, and 7 T when the sample’s doping was set so that $T_c = 16.5$ K. (b) The fluctuation induced magnetoconductivity plotted versus magnetic field for five different temperatures (from bottom to top): 17.0, 17.2, 17.5, 18.0, and 19.0 K. The solid lines are determined from the theory of Dorin et al. [94] using $J = 60$ K, $\tau = 9$ fs, and $\tau_\phi = 7.5$ ps, and appear to capture the field dependence of the data quite well.

where $\rho_0$, $A$ and $c$ are positive constants. While modelling the normal state resistivity is quite straightforward, it turns out that modelling the fluctuation conductivity is more difficult.

### 8.2.2 Fluctuation conductivity

Measurements of the fluctuation conductivity are inherently difficult to perform. The fluctuation (or excess) conductivity is modelled as a paraconductivity acting in parallel with the normal state resistivity. This means that the normal state resistivity must be known in order to determine the excess conductivity. In conventional materials the measurements are usually performed at low temperatures in a regime where the normal state conductivity is temperature independent. However, in underdoped YBa$_2$Cu$_3$O$_{6+x}$ the low-$T$ limit is tem-
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Temperature dependent due in part to the \( \ln(1/T) \) upturn, so other methods must be used to determine \( \rho_n \).

There are a number of methods for dealing with the temperature dependence of the normal state resistivity. One common method is to suppress superconductivity using high magnetic fields and thereby measure the normal state resistivity directly. There are a number of issues related to this approach. For instance the material being studied should have little or no magnetoresistance. Also, in many high-\( T_c \) materials and even in very under-doped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \), a significant field strength would be necessary to fully suppress superconductivity. In our lab we only have access to a 7 T magnet, so full suppression of superconductivity is not possible. However, by performing measurements in lower fields we can study the fluctuation induced magnetoconductivity \( \Delta \sigma(T, H) \):

\[
\Delta \sigma(T, H) = \sigma(T, H) - \sigma(T, 0) = 1/\rho(T, H) - 1/\rho(T, 0).
\] (8.2)

A significant advantage of this approach is that the normal state conductivity cancels out in the subtraction, so the excess conductivity can be determined even if \( \rho_n \) is unknown. Finally, in our experiments we have measured the resistivity at a number of different dopings in the same sample, including one doping where \( T_c \) has been pushed down to zero kelvin. At this doping, however, there are still some superconducting fluctuations, so while we cannot actually measure the normal state resistivity directly, we can make a plausibility argument for our choice for the form of \( \rho_n \).

The in-field resistivity of the YBCO ellipsoid was measured at a doping with \( T_c = 16.5 \) K by Xiaoqing Zhou. Measurements were performed at temperatures from 1 to 50 K and fields of 0.25, 0.5, 1, 3, 5, and 7 T as shown in Figure 8.6a. We can use these data to study the fluctuation induced magnetoconductivity \( \Delta \sigma(T, H) \).

The fluctuation induced magnetoconductivity is plotted versus magnetic field for a five temperatures above \( T_c \) in Figure 8.6b. Also plotted are calculations using the theory of Dorin et al. [94] with \( J = 60 \) K, \( \tau = 9 \) fs, and \( \tau_\phi \) = 7.5 ps. The theoretical curves are not fits to the data, but rather designed to show that in order to achieve reasonable agreement, \( \tau_\phi \gg \tau \). This is further exemplified in Figure 8.7, where the theoretical excess conductivity is plotted for various values of \( \tau \) and \( \tau_\phi \), showing that in order to model the data \( \tau_\phi \) must indeed be much larger than \( \tau \).
Figure 8.7: Calculations of the field dependence of the excess conductivity at 17 K for a $T_c$ of 16.5 K plotted for various values of $\tau$ and $\tau_\phi$ and $J = 76$ K. (a) $\tau = 1$ fs, (b) $\tau = 10$ fs and (c) $\tau = 100$ fs. In all three plots the red curve is for $\tau_\phi = 1$ fs, the orange curve is for $\tau_\phi = 10$ fs, the green curve is for $\tau_\phi = 100$ fs, the blue curve is for $\tau_\phi = 1$ ps, and the purple curve is for $\tau_\phi = 10$ ps.

Looking at the temperature dependence of the field dependent excess conductivity, plotted for all measured field strengths in Figure 8.8a, we see that reasonable agreement at low temperature is possible only if, again, $\tau_\phi \gg \tau$, and if $\tau_\phi$ is allowed to vary dramatically as a function of magnetic field. Notice also that the theory does not agree with the temperature dependence at higher temperatures.

Finally, we fit to the temperature dependence of the resistivity as shown in Figure 8.8b using Equation 8.1 in parallel with the excess conductivity derived by Dorin et al. [94]. These fits were performed to only the data below 30 K with the parameter $A$ in Equation 8.1 set to zero, $c$ set to $1.4 \times 10^{-6}$ and $\rho_0$ used as a fitting parameter. Further, the parameter $J$ in the Dorin theory was set to 76 K while $\tau$ and $\tau_\phi$ were used as fitting parameters. In these fits $\tau$ was found to vary between 0.5 and 1.5 fs while $\tau_\phi$ varied from 40 to 150 ps, again showing a huge discrepancy in the magnitude of the two parameters.

The fits shown in Figure 8.5a use Equation 8.1 in parallel with $a\sigma_{LD}$, where $\sigma_{LD}$ is defined in Equation 4.6 and $a$ is a constant. This temperature dependence for the fluctuations provides an excellent fit to the data, however, the constant $a$, which should in theory be equal to one, ranges from 5–8. It seems that two-dimensionality is important in underdoped
Figure 8.8: (a) The field-dependent excess conductivity at six different fields — 0.25 (black), 0.5 (red), 1 (orange), 3 (green), 5 (blue), and 7 T (purple) — plotted versus temperature. Solid lines are fits to the data at $B = 1$, $3$, and 7 T), using the theory of Dorin et al. [94]. Fit parameters are: for $B = 1$ T, $J = 76$ K, $\tau = 1.6$ fs and $\tau_\phi = 53$ ps; for $B = 3$ T, $J = 76$ K, $\tau = 2.0$ fs and $\tau_\phi = 14$ ps; and for $B = 7$ T, $J = 76$ K, $\tau = 3.1$ fs, and $\tau_\phi = 3.2$ ps. (b) Fits to the temperature dependence of the $ab$-plane resistivity below 30 K using the Dorin theory in parallel with Equation 8.1. The parameters $A$, $c$, and $J$ were held constant for all dopings while $\rho_0$, $\tau$ and $\tau_\phi$ were allowed to vary.

$\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ since these fits do the best job of capturing the temperature dependence of the resistivity. The fits using the Dorin theory require and extraordinarily long phase pair-breaking time, implying long lived fluctuations. These long lived fluctuations could be indicative of preformed pairs, or of a need to extend current theories in order to properly account for the excess conductivity of underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. 
Chapter 9

Currents flowing along the $c$ axis

In order to induce current to flow along the ellipsoid’s crystalline $c$ axis the sample was rotated $90^\circ$ with respect to the axis of the microwave cavity. In this orientation the closing of current loops forces current flow within the $ab$ plane as well. However, since the $c$ axis resistivity is about four orders of magnitude larger than the $ab$-plane resistivity (and the penetration depth is two orders of magnitude larger) the contribution from the $ab$ plane is negligible. For this series of measurements the $T_c$ again started at about 17 K. Room temperature annealing was then used to lower the $T_c$, and 13 dopings were measured as $T_c$ again relaxed to below 3 K.

9.1 Raw data

The raw $c$-axis bandwidth shift data have been scaled by the resonator constant $\Gamma$ to be in surface impedance units ($\Omega$) and are plotted in Figure 9.1 as a function of temperature at all thirteen dopings that were studied. In the normal state we see non-metallic temperature dependence and near $T_c$ there is a large asymmetric peak in the loss. This peak does not appear to be a Josephson plasma resonance but rather appears to be caused by fluctuations as will be discussed in more detail below. Also notice that our 1K pot was not working properly during this series of experiments and so we only have data down to 4.2 K for many of the datasets.

The raw $c$-axis frequency shift data are also scaled to be in ohms and are plotted versus temperature for all thirteen measured dopings in Figure 9.2. In the normal state the fre-
Figure 9.1: The $c$-axis bandwidth shift data scaled to units of ohms and plotted as a function of temperature at all thirteen measured dopings. Inset: a zoomed-in look at the peak near $T_c$ at the highest doping. This peak near $T_c$ does not appear to be a Josephson plasma resonance, but rather a fluctuation peak. The source of the small shoulder below $T_c$ is unknown.

Figure 9.2: The $c$-axis frequency shift data are temperature independent in the normal state because the normal-state skin depth is larger than the sample radius. Thus there is full field penetration, leading to a uniform field within the sample.
Figure 9.3: The real part of the c-axis conductivity shows what is likely a fluctuation peak at \( T_c \). The inset shows the real and imaginary parts of the conductivity. That they cross near the peak in \( \sigma_1 \) lends credence to the idea that the peak is fluctuation related.

The frequency shift is constant because the c-axis skin depth is larger than the sample radius, and so the magnetic field is uniform throughout the sample. This makes analysis of the c-axis data much more difficult, as the raw data are no longer proportional to the complex surface impedance. Instead we are measuring an effective penetration depth \( \lambda_{\text{eff}} \). Determining how \( \lambda_{\text{eff}} \) is related to \( \lambda \) is the subject of Broun and Huttema [4], a summary of which is presented in Appendix A.

### 9.2 Conductivity

The real part of the conductivity, \( \sigma_1 \), is shown in Figure 9.3 and the imaginary part is plotted as \( 1/\lambda^2 \) in Figure 9.4. There is a large fluctuation peak in \( \sigma_1 \) at \( T_c \). If the fluctuation peak is ignored, the conductivity appears to increase smoothly through \( T_c \) and continues to increase down to the lowest temperatures at which I performed measurements. The fluctuation peak is not symmetric about \( T_c \) as seen in the inset to Figure 9.3 and there is a shoulder on the low temperature side of \( T_c \). This shoulder appears in nearly all of the data, although at the
Figure 9.4: (a) The $c$-axis superfluid density $\rho^c_s$ shows power law behaviour. The solid line is a fit to the low temperature data at the highest doping using $A - BT^{2.6}$. Note that the 1K pot in our microwave magnetic field probe was not working during the acquisition of a number of these data sets.

lower dopings the increased width of the main peak tends to reduce the prominence of the shoulder. The source of the shoulder is unknown at this time, but several possibilities can be eliminated. It is not an artefact of the conductivity analysis since there is also a hint of this feature in the raw data, as can be seen in the inset to Figure 9.1. Another possibility that we considered is that it may be a finite-size effect occurring where the penetration depth becomes smaller than the sample radius; however, by looking closely at the penetration depth data we find that this cross-over occurs closer to $T_c$ than does this feature.
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Figure 9.5: The c-axis resistivity shows insulating behaviour throughout and a large fluctuation region. Since no data was taken in a magnetic field the form of the normal state resistivity could not be determined and no fits to the data were performed. The discontinuity in the plot of lowest doping data is there because I have no data in that range of temperature.

9.3 Superfluid density

The c-axis superfluid density $\rho_{s}^{c}$, shown in Figure 9.4, shows a power-law behaviour at low temperatures indicating that the nodes characteristic of a $d$-wave energy gap are governing the low temperature properties. If a phase transition to another state with a gap opening at the nodes had occurred, one would see an exponentially activated temperature dependence at low temperatures. The power law is close to $T^{2.5}$, which has been seen previously at these dopings [70] and is very close to that seen at higher dopings in YBa$_2$Cu$_3$O$_{6+x}$ [126]. Although I have not performed detailed fits using the theory described in Section 3.2, my data are very similar to data that were previously fit using this theory [69].
9.4 Resistivity

Taking the inverse of the $c$-axis conductivity shown in Figure 9.3 produces the $c$-axis resistivity which is plotted in Figure 9.5. The data shows insulating behaviour throughout the temperature range that was studied and a large fluctuation region near $T_c$. Unfortunately, since no measurements of $c$-axis currents were performed in a magnetic field, it is very difficult to determine the correct form for the normal state resistivity. It is thus nearly impossible to implement any fitting procedure to the temperature dependence of the fluctuations, leaving us simply with the observation the the fluctuations are large.
Chapter 10

Gap spectroscopy

Perhaps one of the most controversial issues associated with the cuprates is the structure of the superconducting gap. Our measurements are able to address two aspects of the gap, namely the steepness of its nodal slope, which is related to the nodal velocity $v_\Delta$, and its maximum value $\Delta_0$. The nodal velocity $v_\Delta$ is a principal parameter in determining the thermodynamic properties of low energy $d$-wave quasiparticles. We will attempt to use the temperature dependence of the $ab$-plane superfluid density to infer the doping dependence of $v_\Delta$. However, charge currents are known to be renormalized by various interaction effects, making it difficult in practice to unambiguously assign the observed temperature dependence of the superfluid density to $v_\Delta$. To gain further insight into the relevant physics, we will then turn to $c$-axis superfluid density measurements, in which the renormalization of quasiparticle currents is likely to be much weaker.

In addition we are able to make estimates of the superconducting gap maximum $\Delta_0$. We use two separate analyses, one based on sum-rule arguments applied to the in-plane conductivity, the other based on the $I_cR_N$ product of the intrinsic $c$-axis Josephson junction. The results of the two analyses agree well and provide strong evidence for a small superconducting gap that scales with $T_c$ in the usual BCS way.

10.1 Temperature slope of the superfluid density

The temperature dependencies of the in-plane and out-of-plane superfluid densities are emphasized by looking at the paramagnetic part of the screening response, defined as the
normal fluid density $\rho_n(T) \equiv 1/\lambda^2(T \to 0) - 1/\lambda^2(T)$. The paramagnetic response is sensitive to the energy spectrum of the nodal quasiparticles and directly probes their current response. As can be seen in Figure 10.1, both the in-plane and out-of-plane paramagnetic responses fan out with doping. However, while the out-of-plane normal fluid density shows a decreasing coefficient with increasing doping, the in-plane normal fluid density shows an increasing slope with increasing doping. Note that the out-of-plane normal fluid density is plotted versus $T^{2.5}$ to emphasize the character of the temperature dependence.

### 10.1.1 ab-plane

The $ab$-plane superfluid density is linear in temperature between roughly 5 K and $T_c$, and it is in this region that the slope can be used to probe nodal quasiparticle properties as it
Figure 10.2: Temperature slope of the superfluid density as determined from our penetration depth measurements and from measurements of $H_{c1}$ by Liang et al. [127]. The slope appears fairly constant at higher dopings before diving to zero as $T_c \to 0$.

should correspond to Equation 3.1, i.e:

$$\frac{d}{dT} \left( \frac{1}{\lambda_{ab}^2} \right) = \frac{2 \ln 2}{\pi} \frac{k_B}{\hbar^2} \frac{1}{d} \frac{v_F}{v_\Delta}.$$  

We have already shown in Section 7.3 that the crossover to $T^2$ behaviour in the $ab$-plane superfluid density is consistent with a small amount of pair-breaking in an otherwise pure $d$-wave superconductor. Thus the slope of the the linear term between 5 K and $T_c$ appears as though it would be the limiting low temperature slope if all disorder could be removed. This slope is plotted versus $T_c$ in Figure 10.2; the slope drops quickly to zero as $T_c$ goes to zero. Also plotted in Figure 10.2 is the temperature slope of the first critical field $H_{c1}$ as
measured by Liang et al. [127]. \( H_{c1}(T) \) is related to the penetration depth by

\[
H_{c1} = \frac{\Phi_0 [\ln(\kappa) + 0.5]}{4\pi \lambda_{ab}^2},
\]

where \( \Phi_0 = \hbar/2e \) is the flux quantum and \( \kappa = \lambda_{ab}/\xi_{ab} \), with \( \xi_{ab} \) being the \( ab \)-plane coherence length. Since \( \kappa \) only varies from 40 to 75 in YBa\(_2\)Cu\(_3\)O\(_{6+x}\) when \( T_c \) changes from 10 to 90 K [128], \( \ln(\kappa) \) is nearly independent of doping and \( H_{c1} \) is proportional to the superfluid density. Thus the strength of the temperature dependence of the \( ab \)-plane superfluid density appears to vary little for \( T_c \)'s above 20 K, but below a \( T_c \) of 20 K it drops rapidly to zero.

In a vanilla \( d \)-wave superconductor, the slope of the superfluid density is determined only by the ratio \( v_F/v_\Delta \). We know that \( v_F \) is nearly constant [73], so in order for \( v_\Delta \) to be responsible for the doping dependence of the slope it must be diverging. This is unphysical and is not supported by other measurements [129]. A modification to the theory of the the superfluid density by Millis et al. [59] includes a charge-current renormalization factor \( \alpha \) in the definition of the current (see Chapter 3) that appears as an \( \alpha^2 \) in the temperature dependence of the superfluid density. If the nodal slope is not diverging, then this charge-current renormalization factor may be able to account for the doping dependence of the slope.

### 10.1.2 \( c \)-axis

To further test the nature of \( T_c \rightarrow 0 \) transition, we return our attention to the data from the \( c \)-axis measurements, which show qualitatively different behaviour for the doping dependence of the temperature coefficient. Before going ahead, it is worth reviewing why the \( c \)-axis penetration depth would have a different temperature exponent. This has most notably been discussed by Sheehy et al. [69] who have proposed a model where the Josephson tunnelling between the \( d \)-wave superconducting layers moves from momentum conserving at high temperatures to non-conserving at low temperature. This change in the nature of the tunnelling changes the temperature exponent of the superfluid density \( \beta \) from 1 to 3 (see Section 3.2 and the inset of Figure 10.3). It is reasonable that we see a single value of \( \beta \) in
Figure 10.3: The $c$-axis superfluid density plotted versus $T^{2.5}$. The solid lines are fits to the low temperature behaviour. Inset: The temperature exponent of the $c$-axis superfluid density, $\alpha(\tau)$ (our $\beta$), may vary between 1 and 3, where $\tau = T/\sqrt{v_F v_\Delta \Lambda}$ and $\Lambda$ is an inverse length scale measuring the degree of momentum nonconservation.

our temperature range as $\beta$ is a weak logarithmic function of temperature.

It is understandable that we see a $T^{2.6}$ temperature dependence over much of the temperature range based on our parameters. This is emphasized in Figure 10.3 where the $c$-axis superfluid density is plotted versus $T^{2.6}$. While the temperature dependence is not exactly $T^{2.6}$ for all dopings and temperatures, this plot still provides a useful method for measuring the strength of the temperature dependence through the slope of the fits shown in Figure 10.3. We label this slope $m_{\rho_c}$. From the plot in Figure 10.4a we can see that the temperature slope of the $c$-axis superfluid density appears to be diverging as $T_c \rightarrow 0$. As stated in Section 3.2, the strength of temperature dependence of the $c$-axis superfluid density...

---

Figure 10.4: (a) The strength of the $T^{2.6}$ term in the $c$-axis superfluid density diverges as $T_c \to 0$. (b) From $m_{\rho c}$ and $\beta$ the $T_c$ dependence of $v_\Delta$ can be estimated using Equation 10.3. It appears that $v_\Delta$ is going to zero as $T_c \to 0$.

density is expected to be

$$m_{\rho c} \propto \frac{t_\perp^2}{\sqrt{v_F v_\Delta^{\beta+1}}}.$$  \hspace{1cm} (10.3)

We expect little variation in $t_\perp$ with doping and $v_F$ is known to vary little with doping [130], implying that $v_\Delta \to 0$ as $T_c \to 0$ as shown in Figure 10.4b. When combined with the results from the $ab$-plane superfluid density, this implies that $\alpha^2$ must go to zero even more quickly than $v_\Delta$ is going to zero.

### 10.1.3 Discussion

There are several scenarios in which a strong doping dependence of $\alpha$ would be expected. Within the conventional Fermi liquid framework of the superconducting state, weak residual interactions cause an excited quasiparticle to drag along other quasiparticles, screening its charge and reducing the electrical charge it carries [59, 60]. Charge renormalization is also required to occur in some non-Fermi-liquid theories of the underdoped cuprates, such
as the slave-boson gauge theories originating from Anderson’s resonating valence bond model [58, 131–135]. These models absorb the Coulomb interaction into a rigorous constraint of no double occupancy, and implement the constraint by introducing spinons and holons, new particles that live in two dimensions and carry the spin and charge of the physical electrons separately. In the superconducting state, the spinon and holon are recombined into an electron-like quasiparticle, but with an effective charge that shrinks to zero on underdoping. These theories predict \( \alpha^2 \sim \rho_s^2 \), a result also obtained in theories of fluctuating \( d \)-wave superconductors [76, 78, 80], which may explain the apparent \( \alpha^2 \propto T_c^2 \) dependence seen in Figure 10.2 as \( T_c \propto \rho_s \) at most of the dopings we studied.

In summary, an analysis of the slope of the temperature dependencies of the in-plane and out-of-plane superfluid densities reveals that the nodal gap slope is going to zero with underdoping, while the charge-current renormalization factor also goes rapidly to zero as \( T_c \) approaches zero.

## 10.2 Size of the superconducting gap

Numerous experiments on cuprate high temperature superconductors reveal evidence for two different energy gaps: a normal state pseudogap that grows on underdoping; and a superconducting gap connected to the transition temperature \( T_c \) [136]. In this chapter we use two different experiments to probe the superconducting energy gap scale in underdoped \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \): intrinsic pair tunnelling perpendicular to the \( \text{CuO}_2 \) planes; and measurements of in-plane superfluid spectral weight.

### 10.2.1 Intrinsic \( c \)-axis pair tunnelling

Since the \( c \)-axis electrodynamics are controlled by intrinsic Josephson tunnelling, a measure of the magnitude of the superconducting gap can in principle be determined via the \( I_c R_N \) product: i.e. from the product of the \( c \)-axis critical current and the \( c \)-axis normal state resistance. This can be seen explicitly in the following: it has been shown that the \( c \)-axis penetration depth can be expressed in terms of a Josephson critical current density \( J_c \) [137, 138] as

\[
\frac{1}{\lambda_c^2} = \frac{2\mu_0 d e J_c}{h},
\]  

(10.4)
where $d$ is the spacing between superconducting planes. At low temperatures we expect

$$J_c = \frac{\pi \sigma_n^c \Delta_0}{2\sqrt{2}de}, \quad (10.5)$$

where $\sigma_n^c$ is the normal state conductivity near $T_c$, and $\Delta_0$ is the gap maximum. Rearranging these two equations allows us to extract the magnitude of the gap,

$$2\Delta_0 = \frac{2\sqrt{2} h\omega \sigma_2^c(T \to 0)}{\pi \sigma_n^c}, \quad (10.6)$$

where $\sigma_2^c(T \to 0) = 1/\omega \mu_0 \lambda_\omega^2(T \to 0)$ is the zero-temperature limit of the superfluid density. The $c$-axis normal state resistivity is shown in Figure 9.5. In order to obtain $2\Delta_0$ we chose $\sigma_n^c$ to be the inverse of the maximum value of the measured resistivity. We then choose $\sigma_2^c(T \to 0)$ to be the $T^{2.6}$ extrapolation of $\rho_s^c$ to $T = 0$. Using these values Equation 10.6 yields the data points shown on Figure 10.5 as blue circles.

### 10.2.2 In-plane superfluid spectral weight

An estimate of the magnitude of the superconducting gap can also be made using spectral weight arguments applied to the $ab$-plane measurements. In this case, we are asking the question, ‘up to what energy must spectral weight be drawn from the optical conductivity $\sigma(\omega)$ in order to form the observed zero-temperature superfluid density?’ As shown in Section 2.4, this requires a knowledge of the form of $\sigma(\omega)$ in the normal state. Since the normal state scattering rate is much larger than both the superconducting gap and our measurement frequency, it is a reasonable first step to assume that $\sigma(\omega)$ is frequency independent in the range we are interested in, and has a value given by the dc normal state conductivity. This in essence assumes that superconductivity originates from a normal state in the dirty limit, $h/\tau \gtrsim k_B T_c$, but this is well supported by other measurements on transport and optics [139]. In this case the connection between $\Delta_0$, $\rho_s$ and $\sigma_N$ is given by Equation 2.30:

$$2\Delta_0 \approx \frac{h\omega \sigma_2(T \to 0)}{\sigma_N}. \quad (10.7)$$
Figure 10.5: The superconducting gap $2\Delta_0$ versus $T_c$ as determined by Equation 10.6 for $c$-axis intrinsic pair tunnelling and Equation 2.30 for $ab$-plane superfluid spectral weight. The two independent estimates of $\Delta_0$ show a similar dependence on $T_c$ that is nearly equal to what is expected from BCS theory.

Taking the zero-temperature superfluid density to be the extrapolation of the $ab$-plane superfluid density to zero temperature and the normal state resistivity to be the value of the resistivity at 40 K leads to the gap magnitude plotted in Figure 10.5 as red crosses. The magnitude of the gap as determined by these two different measurements is remarkably similar and nearly linear in doping, with a slope $2\Delta_0 \approx 4k_B T_c$, which is very close to the BCS $d$-wave value.
Chapter 11

Conclusion

This thesis has focused on making high quality electrodynamic measurements in an interesting and little studied part of the cuprate phase diagram, at the underdoped edge of the $d$-wave superconducting dome. These measurements were made possible by the preparation of highly homogeneous samples by Ruixing Liang and co-workers at the University of British Columbia, and our collaborative development of a technique for continuously tuning of hole doping in a single sample over a 20 K range of $T_c$.

The central outstanding issues in the cuprates mainly concern the nature of the cuprate normal state, which can neither be determined from first principles calculations nor inferred from any single measurement. The results reported in this thesis shed light on this issue in several ways: by examining the extent to which nodal $d$-wave quasiparticles are perturbed by competing or coexisting electronic orders; by studying the nature of the transition from superconducting to nonsuperconducting state, both at low temperature as a function of doping (quantum phase transition) and at fixed doping as a function of temperature (thermal transition); by probing the energy scale for the superconducting condensate using powerful arguments based on the oscillator strength sum rule applied to in-plane and out-of-plane experiments; and by attempting to build a consistent phenomenology of the nodal quasiparticles, in terms of parameters such as the nodal velocity $v_{\Delta}$. This last point has exposed another piece of physics that bears on the issue of the nature of the normal state, suggesting a strong doping dependence of the effective charge carried by nodal quasiparticle currents.
Competing/coexisting orders

The measurements of in-plane superfluid density reported here generically show that the superfluid density crosses over from a quadratic temperature dependence at low temperatures to $T$-linear at higher temperature. This temperature dependence is consistent with pure $d$-wave superconductivity in the presence of a small amount of pair-breaking disorder and we are able to rule out BCS-BEC crossover physics; competition from $d_{x^2+y^2} + is$ superconductivity; and spin and charge-density waves that nest the nodal points. Due to the presence of disorder, we cannot eliminate completely the possibility of either disordered $d_{x^2+y^2} + id_{xy}$ superconductivity or a perturbation from a $\Theta_{II}$-type circulating current phase, but we can place sufficiently tight limits on these that they cannot be playing an important role in the overall physics of the cuprates.

Quantum and thermal phase transitions

The nature of the quantum phase transition from superconductor to nonsuperconductor can be probed by studying the doping dependence of the zero temperature superfluid density. $\rho_{s0}$ displays the behaviour expected for a quantum phase transition in the (3+1)-dimensional $XY$ universality class, with $\rho_{s0} \propto (p - p_c)$, $T_c \propto (p - p_c)^{1/2}$ and $\rho_s(T) \propto (T_c - T)^1$ as $T \rightarrow T_c$. The nature of the thermal transition is probed in two ways. First, while optimally and slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ display critical fluctuations in the 3D-$XY$ universality class, at none of our dopings do we see signs of critical fluctuations as $T \rightarrow T_c$. Instead the transition is mean-field-like and there is no indication of vortex unbinding. Second, the form of the excess conductivity above $T_c$ has a temperature dependence that is consistent with the Lawrence-Doniach theory with a crossover from two-dimensional fluctuations well above $T_c$, to three-dimensional fluctuations near $T_c$. However, the magnitude of these fluctuations is 5–8 times larger than expected. An attempt to model the magnitude of the effect using the theory of Dorin at al. points strongly to an anomalously large dephasing time for the superconducting fluctuations. This may have important implications for the theories that view the cuprate pseudogap region in terms of phase disordered superconductivity.
CHAPTER 11. CONCLUSION

Superconducting energy scales

Many experiments have shown the existence of two different energy scales in the underdoped cuprates. One is associated with the high temperature pseudogap and the other tracks the superconducting transition temperature. We have deduced a gap magnitude in two different ways with our measurements. Within the $ab$-plane, conductivity spectral weight arguments allow the gap magnitude to be determined from the ratio of the zero temperature superfluid density and the normal state resistivity. Along the $c$-axis, the mechanism for conduction is very different and is described in terms of Josephson tunnelling between layers. This allows an independent determination of the gap magnitude from the $I_c R_n$ product. Both of these techniques produce a magnitude for the superconducting gap that varies linearly with doping with a magnitude close to expectations for a $d$-wave BCS superconductor, $2\Delta_0 \approx 4k_B T_c$.

Nodal quasiparticle phenomenology

The excitation spectrum of nodal quasiparticles in a $d$-wave superconductor is parameterized by two numbers, the Fermi velocity $v_F$ and the gap velocity $v_\Delta$. An additional parameter, the charge-current renormalization factor $\alpha$, should also enter the description of the $ab$-plane superfluid density. In this work, a combination of in-plane and $c$-axis measurements has revealed that $v_\Delta$ most likely has a weak doping dependence, shrinking slightly as $T_c \to 0$. The charge-current renormalization factor, however, has a strong doping dependence, with charge currents eventually becoming neutral as $T_c \to 0$. These observations have important implications for gauge theories of cuprate superconductivity.
Appendix A

Effective penetration depths

When measuring the $c$-axis properties of a sample the results will always contain an admixture of the $ab$-plane properties, since the current must flow in closed loops. The sample of interest in this thesis is ellipsoidal in shape and is highly electrically anisotropic. The $c$-axis penetration depth is roughly 100 times larger than the $ab$-plane penetration depth and the $c$-axis resistivity is roughly 10,000 times larger than that of the $ab$-plane. Additionally, the normal state skin depth along the $c$-axis is larger than the dimensions of the sample, leading to what are known as “finite size effects", while the zero temperature $c$-axis penetration depth is much smaller than the sample dimensions, which greatly complicates the analysis of the measurements of the $c$-axis properties. The full analysis of the finite size effects in highly anisotropic cylinders and spheres is developed in Broun and Huttema [4]. I will present a brief summary of our findings here.

In our sample the London penetration depth is, in Cartesian coordinates, a diagonal tensor with elements $(\lambda_{ab}, \lambda_{ab}, \lambda_c)$. The London screening equation, Equation 2.10, can then be rewritten as

\[
\begin{pmatrix}
H_x \\
H_y \\
H_z
\end{pmatrix} = \begin{pmatrix}
\lambda_c^2 (\partial_{yy}H_x - \partial_{xy}H_y) + \lambda_{ab}^2 (\partial_{zz}H_x - \partial_{xz}H_z) \\
\lambda_{ab}^2 (\partial_{zz}H_y - \partial_{yz}H_z) + \lambda_c^2 (\partial_{xx}H_y - \partial_{xy}H_x) \\
\lambda_{ab}^2 (\partial_{xx}H_z - \partial_{xz}H_x) + \lambda_{ab}^2 (\partial_{yy}H_z - \partial_{yz}H_y)
\end{pmatrix},
\]

where, for instance, $\partial_{xy}$ denotes the partial derivative $\frac{\partial^2}{\partial x \partial y}$ and so on.

Dissipative electrodynamics at finite frequencies can also be treated in the above frame-
work as the static screening response in the Meissner state by replacing the static electromagnetic fields with harmonically varying quasistatic fields, represented in phasor notation. For example,

\[ H \rightarrow H(t) = \text{Re} \left\{ \tilde{H} e^{i\omega t} \right\}. \]  

(A.2)

In this case, the penetration depth \( \lambda \) is replaced with a complex skin depth \( \tilde{\delta} \) that is determined by the complex conductivity,

\[ \sigma = \sigma_1 - i\sigma_2 = \frac{1}{i\omega \mu_0 \tilde{\delta}^2}. \]  

(A.3)

Thus the surface impedance is is \( Z_s = R_s + iX_s = i\omega \mu_0 \tilde{\delta}. \)

In order to determine the effective penetration depth for our ellipsoidal sample, the shape was approximated by a sphere. The radius of the sphere was set by measuring the mass of the sample and, knowing the density of the \( \text{YBa}_2\text{Cu}_3\text{O}_{6.333} \), calculating the volume of sample necessary to produce its mass. By assuming this volume was spherical, it was
determined that the average radius of the sample is \( a = 183 \pm 5 \mu m \). The solution to the problem of the electrically anisotropic sphere was determined in the limit \( \lambda_{ab} \to 0 \) by carrying out multipole expansions of the interior and exterior magnetic fields and matching them at the surface of the sphere. The key to making this process tractable is to use the somewhat unusual choice of coordinate systems shown in Figure A.1, in which the external field is applied along the \( x \) direction and the crystal \( c \) axis points in the \( z \) direction, with cylindrical coordinates used inside the sphere and spherical coordinates outside. The internal solutions are then of the form

\[
H^\text{int}_\rho(\rho, \phi, z = a \sin \theta) = \frac{h(\theta) a \sin \theta I_1(\rho/a)}{\rho I_1(a \sin \theta/a)},
\]

(A.4)

where \( h(\theta) \) is the field at the surface and \( I_\nu(x) \) are modified (or \textit{hyperbolic}) Bessel functions of the first kind, of order \( \nu \). The external field is a solution of \( \nabla^2 H = 0 \) and there is no current, so the external field can be obtained from a scalar potential, \( H^\text{ext} = -\nabla \Phi_m \). The solution outside the sphere is then written in terms of the magnetic scalar potential as

\[
\Phi_m = -H_0 r \sin \theta \cos \theta + \sum_{\text{odd } \ell} \frac{c_\ell P^1_\ell(\cos \theta) \cos \phi}{r^{\ell+1}},
\]

(A.5)

where \( P^m_\ell(x) \) are the associated Legendre polynomials. Equating internal and external fields leads to the solution

\[
\frac{4}{3} H_0 \delta_{\ell,1} = \frac{2\ell(\ell+1)^2}{2\ell+1} \frac{c_\ell}{a^{\ell+2}} + \sum_{\text{odd } \ell'} \frac{c_\ell}{a^{\ell+2}} (\ell' + 2) \langle \ell | g^{-1}(x) | \ell' \rangle,
\]

(A.6)

where

\[
\langle \ell | g^{-1}(x) | \ell' \rangle = \frac{\lambda_c}{a} \int_0^\pi \frac{P^1_\ell(\cos \theta) I_1(a \sin \theta/\lambda_c) P^1_{\ell'}(\cos \theta)}{I_2(a \sin \theta/\lambda_c)} d\theta.
\]

(A.7)

In practice the problem is solved numerically by truncating the sum over \( \ell \) at some finite \( \ell = \ell_{\text{max}} \) and solving a linear system for \( c_\ell \). The solutions converge rapidly with \( \ell_{\text{max}} \), and in practice only five or so terms are required.
Appendix B

Dealing with admixtures

Ideally, when measuring the $ab$-plane response, there would be perfect alignment of the sample’s crystalline $c$-axis and the symmetry axis of the microwave magnetic field. This would induce currents to flow wholly within the plane. Our main alignment tool was the residual flat surfaces of the $ab$ plane platelet that the ellipsoid was cut and polished out of. These flat surfaces are parallel to each other and perpendicular to the crystal’s $c$ axis. Thus, resting the sample on one of these faces on the end of the sapphire sample holder aligns the $c$ axis nearly along the microwave magnetic field.

For the $c$-axis measurements the sample was mounted with its $c$ axis perpendicular to the microwave magnetic field. In this orientation we have full field penetration in the normal state. There is also very little effect due to the $ab$-plane, even though the induced current must flow within the plane in order to form a closed loop. This is because the loss from $c$-axis currents is four orders of magnitude larger than for the $ab$-plane and the penetration depth is two orders of magnitude larger. However, this anisotropy does affect measurements of the $ab$-plane response since there is always some misalignment of the microwave magnetic field with respect to the the crystalline $c$-axis. To counteract this, we have used our measurements of the $c$-axis response to apply a small correction to our $ab$-plane data.

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Figure B.1: Laue diffraction image of the YBCO ellipsoid and sapphire sample holder. Sapphire diffraction spots appear as double due to the sample absorbing X-rays. The green lines are drawn along lines of sapphire spots to identify the orientation of the sapphire rod, while the red circles identify spots from the sample and the red lines identify the orientation of the sample. The relative difference between the two crossing points makes up a large portion of the misalignment between the sample and the microwave magnetic field.
Figure B.2: These plots show the effect of the misalignment correction. The raw data is in orange and the corrected data in black. The misalignment correction affects $R^{ab}_s(T)$ and $X^{ab}_s(T)$ differently. (a) $R^{ab}_s$ is mostly affected at low temperatures where $R^{c}_s$ is much larger than $R^{ab}_s$. (b) $X^{ab}_s$ is most strongly affected in the normal state where the measured $X^{c}_s$ is large.

B.1 Misalignment correction

After the $ab$-plane doping sweep was carried out, the sapphire sample holder was removed from the MMP and Laue diffraction was performed to try to determine the orientation of the sample’s $c$-axis relative to the microwave magnetic field. An example diffraction pattern is shown in Figure B.1. Diffraction patterns were produced of the sample on the sapphire sample holder, the sample on its own and the sample holder on its own. This allowed me to identify which spots were produced by which object. The end result was that there appeared to be a $3.1^\circ \pm 0.5^\circ$ misalignment between the sapphire and the sample. There may also be a misalignment between the sapphire rod and the microwave magnetic field, but this is likely to be much smaller as the sapphire rod and the resonator are large compared to the ellipsoid. However, since the sample was not moved during most of the $ab$-plane doping sweep, we can be confident that the misalignment remains constant.
The misalignment affects the measured $ab$-plane surface impedance as follows

$$Z_{s,\text{measured}}^{ab} = \cos^2 \theta Z_s^{ab} + \sin^2 \theta Z_s^c,$$

where $\theta$ is the angle between the crystal’s $c$-axis and the direction of the microwave magnetic field and $Z_s^{ab}$ and $Z_s^c$ are the $ab$-plane and $c$-axis response at the same $T_c$, respectively. Since the $c$-axis response was not measured during the same doping run as the $ab$-plane response and thus was not measured for the same $T_c$’s, it was necessary to interpolate between $c$-axis measurements at $T_c$’s that bracketed the $ab$-plane measurement in question to produce a $c$-axis dataset at the same $T_c$ as the $ab$-plane measurement.

In Figure B.2 the results of the misalignment correction are shown for one dataset. The correction strongly affects the normal state value of $X_s$, and more weakly, the low temperature value of $R_s$. 
Appendix C

Mixed-symmetry superconducting states

The main effect of disorder in a superconductor is for the quasiparticles to acquire a finite lifetime, the magnitude and energy dependence of which depend on the concentration and scattering strength of the defects. Near the unitarity limit, scattering leads to a zero-energy resonance that overlaps with the continuum of quasiparticle states in the $d_{x^2-y^2}$-wave superconductor, resulting in a residual density of states in $N(\omega)$ and a crossover to $T^2$ behaviour in $\rho_s(T)$. This also happens for the $d_{x^2-y^2} + id_{xy}$ superconductor, despite there initially being a finite gap in the excitation spectrum. As a result, above a certain level of disorder, $d_{x^2-y^2}$ and $d_{x^2-y^2} + id_{xy}$ states become impossible to tell apart using microwave spectroscopy. In Figure C.1 we show how the distinction is lost when the energy scale of the disorder, $k_B T_d$ becomes comparable to $\Delta_{d_{xy}}$. The $d_{x^2-y^2} + is$ superconductor is different in this respect: nonmagnetic scatterers do not cause pair breaking at low energies, and the gap in the spectrum is robust.

The $d_{x^2-y^2} + id_{xy}$ state and the $d_{x^2-y^2} + is$ state are two candidate order parameters that may compete with pure $d_{x^2-y^2}$ superconductivity in the cuprates. In this appendix we review the theory of the penetration depth in the presence of disorder and gauge the extent to which these states can be distinguished by microwave experiments. The theory of unconventional superconductivity in the presence of elastic scattering disorder has been developed by many authors [52, 56, 105, 140–145], and has been reviewed in several places [146–148]. In these systems, disorder not only imparts a finite lifetime to the quasiparticles, it alters the excitation spectrum by pair-breaking, and the two effects must be dealt with together. The self-consistent $t$-matrix approximation (SCTMA) provides a powerful
APPENDIX C. MIXED-SYMMETRY SUPERCONDUCTING STATES

approach for capturing this physics, particularly in the resonant scattering limit, where the impurity is on the verge of binding a quasiparticle at the Fermi energy. In the SCTMA, impurities are usually approximated as point defects that scatter in the $s$-wave channel. The effect of the disorder is to renormalize the quasiparticle energy $\omega$ and the superconducting gap $\Delta_k$, which can be expressed in the following way:

$$\omega \rightarrow \tilde{\omega} = \omega + i\pi \frac{N(\omega)}{\epsilon^2 + N^2(\omega) + P^2(\omega)},$$

$$\Delta_k \rightarrow \tilde{\Delta}_k = \Delta_k + i\pi \frac{P(\omega)}{\epsilon^2 + N^2(\omega) + P^2(\omega)}.$$  

Here $\Gamma = n_i n / \pi^2 D(\epsilon_F)$, where $n_i$ is the impurity concentration, $n$ is the conduction electron density, and $D(\epsilon_F)$ is the density of states at the Fermi level [105]. The impurity scattering strength is characterized by $c$, the cotangent of the $s$-wave scattering phase shift. The quasiparticle density $N(\omega)$ and pair density $P(\omega)$ depend on details of the particular superconducting state and are defined below for the different types of order parameter. For purely unconventional order parameters, $\langle \Delta_k \rangle_{FS} = 0$ and $P(\omega)$ vanishes — these states are therefore unrenormalized by $s$-wave scatterers.

We are primarily interested in the behaviour of the low energy excitations so, without loss of generality, we take the two-dimensional Fermi surface to be isotropic, and the gap functions to be the simplest cylindrical harmonics of the required symmetry:

$$\Delta_{d_{x^2-y^2}} = \Delta_0 \cos 2\phi,$$

$$\Delta_{d_{xy}} = \eta \Delta_0 \sin 2\phi,$$

$$\Delta_s = \zeta \Delta_0.$$  

Here $\phi$ measures angle from the Cu–O bond direction and $\eta$ and $\zeta$ are constants. For the pure $d_{x^2-y^2}$ state there is no gap renormalization. The quasiparticle density is

$$N(\omega) = \left\langle \frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 - \Delta_0^2 \cos^2 2\phi}} \right\rangle_{\phi} = \frac{2}{\pi} K \left( \frac{\Delta_0^2}{\tilde{\omega}^2} \right),$$

where $\langle ... \rangle_\phi$ is an angle average around the cylindrical Fermi surface, $K(x)$ is the complete elliptic integral of the first kind, and the branch of the square root in Equation C.6 is chosen.
APPENDIX C. MIXED-SYMMETRY SUPERCONDUCTING STATES

so that \( \tilde{\omega} \) has positive imaginary part. In the strong-scattering (unitarity) limit, for instance, \( c = 0 \) and \( \tilde{\omega}(\omega) \) is a root of

\[
\tilde{\omega} = \omega + i\pi^2/2K(\Delta_0^2/\tilde{\omega}^2).
\] (C.7)

\( \tilde{\omega}(\omega) \) encodes all the physics of scattering and pair-breaking. Inserted into the real part of Equation C.6 it gives the quasiparticle density of states in the presence of disorder. To calculate penetration depth using \( \tilde{\omega} \), a modification of Equation 2.37 is used [105]:

\[
\frac{\lambda_0^2}{\lambda^2(T)} = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \tanh \left( \frac{\omega}{2k_B T} \right) \text{Re} \left( \frac{\tilde{\Delta}_k^2}{(\tilde{\omega}^2 - \Delta_k^2)^{\frac{3}{2}}} \right)_{FS}.
\] (C.8)

The density of states factor is

\[
\left\langle \frac{\tilde{\Delta}_k^2}{(\tilde{\omega}^2 - \Delta_k^2)^{\frac{3}{2}}} \right\rangle_{FS} = \left\langle \frac{\Delta_0^2 \cos^2 2\phi}{(\tilde{\omega}^2 - \Delta_0^2 \cos^2 2\phi)^{\frac{3}{2}}} \right\rangle_{\phi},
\] (C.9)

\[
= \frac{2}{\pi \tilde{\omega}} \left( K(\Delta_0^2/\tilde{\omega}^2) + \frac{\tilde{\omega}^2}{\Delta_0^2 - \tilde{\omega}^2} E(\Delta_0^2/\tilde{\omega}^2) \right),
\] (C.10)

where \( E(x) \) is the complete elliptic integral of the second kind.

For the \( d_{x^2-y^2} + id_{xy} \) state, \( \Delta(\phi) = \Delta_0(\cos 2\phi + i\eta \sin 2\phi) \), and there is similarly no gap renormalization. The quasiparticle density is

\[
N(\omega) = \left\langle \frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 - \Delta_0^2(\cos^2 2\phi + \eta^2 \sin^2 2\phi)}} \right\rangle_{\phi}.
\] (C.11)

\[
= \frac{2}{\pi \sqrt{\tilde{\omega}^2 - \eta^2 \Delta_0^2}} K\left( \frac{(1 - \eta^2) \Delta_0^2}{\tilde{\omega}^2 - \eta^2 \Delta_0^2} \right).
\]
The density of states factor in Eq. C.8 becomes
\[
\left\langle \frac{\tilde{\Delta}_k^2}{(\tilde{\omega}^2 - \tilde{\Delta}_k^2)^{\frac{3}{2}}} \right\rangle_{FS} = \left\langle \frac{\Delta_0^2(\cos^2 2\phi + \eta^2 \sin^2 2\phi)}{(\tilde{\omega}^2 - \Delta_0^2(\cos^2 2\phi + \eta^2 \sin^2 2\phi))^{\frac{3}{2}}} \right\rangle_{\phi} = 2 \frac{1}{\sqrt{\tilde{\omega}^2 - \eta^2 \Delta_0^2}} \left[ K \left( \frac{(1 - \eta^2)\Delta_0^2}{\tilde{\omega}^2 - \eta^2 \Delta_0^2} \right) + \frac{\tilde{\omega}^2}{\Delta_0^2 - \tilde{\omega}^2} E \left( \frac{(1 - \eta^2)\Delta_0^2}{\tilde{\omega}^2 - \eta^2 \Delta_0^2} \right) \right]
\]
(C.12)

In the \(d_{x^2-y^2} + is\) state, impurity renormalization of \(\Delta_s\) must be taken into account. The renormalization equations C.1 and C.2 can be rewritten
\[
1 = \frac{\omega}{\tilde{\omega}} + i\pi \Gamma \frac{N(\omega)/\tilde{\omega}}{c^2 + N^2(\omega) + P^2(\omega)}, \quad (C.13)
\]
\[
1 = \frac{\Delta_s}{\tilde{\Delta}_s} + i\pi \Gamma \frac{P(\omega)/\tilde{\Delta}_s}{c^2 + N^2(\omega) + P^2(\omega)}, \quad (C.14)
\]
where
\[
N(\omega) = \left\langle \frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 - \Delta_0^2 \cos^2 2\phi - \tilde{\Delta}_s^2}} \right\rangle_{\phi}, \quad (C.15)
\]
\[
P(\omega) = \left\langle \frac{\tilde{\Delta}_s}{\sqrt{\tilde{\omega}^2 - \Delta_0^2 \cos^2 2\phi - \tilde{\Delta}_s^2}} \right\rangle_{\phi}. \quad (C.16)
\]
Since \(N(\omega)/\tilde{\omega} = P(\omega)/\tilde{\Delta}_s\), the quantities \(\omega/\tilde{\omega}\) and \(\Delta_s/\tilde{\Delta}_s\) obey identical equations and therefore \(\tilde{\Delta}_s = \Delta_s \omega/\tilde{\omega}\). Equation C.13 and Equation C.14 can then be combined into a single equation
\[
\tilde{\omega} = \omega + i\pi \Gamma \frac{N(\omega)}{c^2 + N^2(\omega)(1 + \Delta_s^2/\omega^2)}, \quad (C.17)
\]
where
\[
N(\omega) = \left\langle \frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 (1 - \Delta_s^2/\omega^2) - \Delta_0^2 \cos^2 2\phi}} \right\rangle_{\phi} = 2 \frac{1}{\pi \sqrt{1 - \Delta_s^2/\omega^2}} K \left( \frac{\Delta_0^2}{(1 - \Delta_s^2/\omega^2)\tilde{\omega}^2} \right). \quad (C.18)
\]
APPENDIX C. MIXED-SYMMETRY SUPERCONDUCTING STATES

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Figure C.1: The onset of quadratic temperature dependence of $\rho_s(T)$ in a $d_{x^2-y^2} + id_{xy}$ superconductor as a function of disorder strength, relative to that of a $d_{x^2-y^2}$ state. $\beta_{d+id}$ is the $T^2$ coefficient of $\rho_s(T)$ for the $d_{x^2-y^2} + id_{xy}$ superconductor. $\beta_d$ is the same quantity for the $d_{x^2-y^2}$ state. Disorder strength is characterized by the disorder crossover temperature $T_d$ of the $d_{x^2-y^2}$ superconductor, as defined in the text. Data are plotted for different values of the $d_{xy}$ gap, $\Delta_{d_{xy}}$, and scale well as a function of $T_d/\Delta_{d_{xy}}$. The two pairing states are difficult to distinguish on the basis of $\Delta \rho_s(T)$ when $k_B T_d \gtrsim \Delta_{d_{xy}}$.

The corresponding term in Equation C.8 is

$$\left\langle \frac{\tilde{\Delta}^2}{(\tilde{\omega}^2 - \Delta_k^2)^{\frac{3}{2}}} \right\rangle_{\text{FS}} = \left\langle \frac{\Delta_0^2 (\cos^2 2\phi + \eta^2 \sin^2 2\phi)}{(\tilde{\omega}^2 - \Delta_0^2 (\cos^2 2\phi + \eta^2 \sin^2 2\phi))^\frac{3}{2}} \right\rangle_{\phi} = \frac{2}{\pi} \frac{1}{\tilde{\omega} \sqrt{1 - \frac{\Delta_k^2}{\tilde{\omega}^2}}} \times$$

$$\left[ K \left( \frac{\Delta_0^2}{(1 - \frac{\Delta_k^2}{\tilde{\omega}^2}) \tilde{\omega}^2} \right) + \frac{\tilde{\omega}^2}{\Delta_0^2 - (1 - \frac{\Delta_k^2}{\tilde{\omega}^2}) \tilde{\omega}^2} E \left( \frac{\Delta_0^2}{(1 - \frac{\Delta_k^2}{\tilde{\omega}^2}) \tilde{\omega}^2} \right) \right].$$

We are now in a position to compare results for the three order parameters. The forms for the density of states $N(\omega)$ and the superfluid density $\rho_s(T)$ are shown in Table 7.1,
both in the clean limit and in the presence of strong scattering disorder \((c = 0)\). The key feature of the clean \(d_{x^2-y^2} + id_{xy}\) and \(d_{x^2-y^2} + is\) states is a finite energy gap, giving rise to activated behaviour in \(\rho_s(T)\). The \(d_{x^2-y^2} + id_{xy}\) and \(d_{x^2-y^2} + is\) states behave very differently in response to disorder. In the \(d_{x^2-y^2} + is\) case, the energy gap is robust. This can be traced back to the expressions for the renormalized frequency, Equation C.17 and Equation C.18. Impurity renormalization of \(\Delta_s\) leads to solutions for \(\tilde{\omega}\) that are purely real for \(\omega < \Delta_s\), preventing the formation of any low-lying quasiparticle states in \(N(\omega)\) [145].

The \(d_{x^2-y^2} + id_{xy}\) case is quite different: pair breaking occurs for even small amounts of disorder, leading immediately to a \(T^2\) term in \(\rho_s(T)\). The \(T^2\) term starts out weak, but grows in magnitude until it is comparable to that of a pure \(d_{x^2-y^2}\) superconductor with a similar amount of disorder. This crossover is plotted in Figure C.1, which shows that the \(d_{x^2-y^2}\) and \(d_{x^2-y^2} + id_{xy}\) states become indistinguishable when the energy scale for the disorder, \(k_B T_d\), becomes comparable to \(\Delta_{d_{xy}}\).
Bibliography


