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16 February, 2000
Electron Diffraction Studies of Amorphous Materials

William Eric McBride

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

SCHOOL OF PHYSICS
THE UNIVERSITY OF SYDNEY
AUSTRALIA

September 1999
To Karin, Emma and Nick.
Authorship

The energy filtered electron diffraction pattern (EFDP) technique reviewed in Chapter 2 is the result of work by a number of different researchers, who have been acknowledged within the text. The plasmon dispersion technique which grew out of the EFDP technique was developed primarily by Dr D.C. Green and Dr D.G. McCulloch. However as this technique relies upon hardware and software developed for the EFDP technique it is difficult to delineate individual responsibilities in the development of this technique. Also, in Chapter 3 a number of different carbon specimens are investigated; these specimens were prepared by Dr D.G. McCulloch, Tony Romeo and the author.

This thesis has not been submitted for a degree at this or any other University, although some of the work presented in this thesis has been published or is currently in press. This work is listed below.


I thank my supervisor, Professor David Cockayne, whose exacting mentorship, particularly during the writing of this thesis, has developed in me skills for life, as well as for research.

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Abstract

This Thesis studies various ways in which electron diffraction can be employed to extend the amount of structural information that is obtainable from amorphous materials. In particular three diffraction based electron-optical techniques, at different stages in their development, are presented. The manner in which these techniques seek to obtain further structural information is through a more thorough utilisation of the information available in electron diffraction patterns and a reduction in the volume of the sample from which this structural information is derived.

Intensity observed in an electron diffraction pattern originates from electrons that have undergone a number of different types of scattering event. In general these can be subdivided into elastic and inelastic scattering events, where an elastically scattered electron exhibits no detectable loss of energy and an inelastically scattered electron has lost some energy. Using energy filtering it is possible to identify elastic and inelastically scattered electrons and to analyse them independently. In this Thesis a technique is presented that analyses inelastically scattered electrons. More specifically this technique investigates a particular type of inelastic scattering event known as the plasmon. Measurements of plasmon behaviour are then used to characterise amorphous materials that have different atomic and electronic structures.

A more standard method for obtaining structural information from amorphous
materials is through the measurement of elastically scattered electrons, from which a reduced density function (RDF) can be determined. The RDF provides accurate information about interatomic spacings in monatomic amorphous and polycrystalline materials, but is restricted in that it reveals only the average structure of the specimen volume illuminated by the electron beam. To overcome this restriction smaller specimen volumes must be illuminated. Unfortunately this often results in the use of convergent illumination which does not satisfy experimental criteria needed to perform RDF analysis. As such, a method is developed which utilises deconvolution techniques to allow RDF analysis to be performed using convergent electron illumination.

Another method by which it is possible to reduce the volume of the sample from which structural information is derived results from the combination of electron diffraction and electron imaging. Using this combination a tilted dark field technique is developed which derives structural information from smaller specimen volumes, by the association of intensity in a dark field image with the volume in the sample from which it was scattered. This volume is dependent on the size of the objective aperture that is employed.
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CHAPTER 1

Introduction

1.1 A Brief History of Electron Diffraction

Electron diffraction has now been used for approximately seventy years as an analytical tool for investigating the structure of materials. During this time, significant improvements have been made to the apparatus used to perform electron diffraction. These improvements have increased the speed and accuracy with which electron diffraction measurements can be made and have also extended the limits of the applicability of electron diffraction. Perhaps one of the main reasons for the enduring popularity of electron diffraction is the broad range of materials that it is capable of analysing. These include gases, crystals, polycrystalline and amorphous solids.

The electron was discovered in 1897 by J.J. Thomson who demonstrated that an electron was a particle with a specific mass and charge. However it was not
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until 1924, when Louis de Broglie presented his doctoral thesis proposing that the wave particle duality of radiation also applied to matter, that the possibility of electron diffraction was conceived. At this time though electron diffraction was only an idea as there was no experimental evidence to support its existence.

Experimental verification came three years later in 1927 in two independent experiments. One experiment was performed by Davisson and Germer [1], who reflected low energy electrons (30-600eV) off the surface of thin crystals of nickel to form an electron diffraction pattern. This experiment marks the beginning for what is presently known as low-energy electron diffraction (LEED). The other experiment was performed by Thomson and Reid [2]; they used higher energy electrons (10-60keV), to transmit electrons through foils of aluminium, platinum and gold to form a diffraction pattern. This experiment was the precursor to what is now called high energy electron diffraction (HEED).

Diffraction is not a phenomenon that is unique to electrons. Visible light, X-rays, neutrons and waves at the beach all exhibit diffraction. In fact, X-ray diffraction was discovered some fifteen years earlier than electron diffraction and consequently much of the early theoretical work used in the development of electron diffraction is borrowed from X-ray diffraction. What makes electron diffraction unique when compared with these other forms of diffraction, some of which can also be used to perform material structural investigations, is the variety of problems to which it can be applied. This versatility is derived from the fundamental physical properties of the electron.

Of all the different physical properties of the electron, perhaps the most significant, in terms of affording electron diffraction its versatility, is the negative charge which the electron carries. The charge on the electron gives the electron a larger scattering cross section than either X-rays or neutrons (both of which are commonly used to perform diffraction experiments and neither of which carry charge). Essentially this means that an electron is more likely to interact with a
material and can thus be used to examine much smaller specimen volumes. However examining small volumes of materials (typically surface areas of 100nm²) was not always thought to be advantageous. One of the early arguments against the usefulness of examining such small volumes of material (note that it is now possible to investigate surface areas of less than 0.04nm²), was that the results could not be used to describe or understand the structure in the bulk of the sample. This argument still holds, to an extent, but repeated comparisons between X-ray, neutron and electron diffraction data have shown that results derived from such small volumes of material can, in many instances, be reliably extrapolated to the bulk of the material.

There are other benefits that are derived from the fact that an electron is a charged particle. They are that an electron can be accelerated, which allows its kinetic energy to be controlled, and more importantly that electrons can be focussed using electrostatic or electromagnetic lenses. The ability to focus electrons has greatly effected the development of electron diffraction and has led to the coupling of electron diffraction to electron imaging (known as electron microscopy) through the facility of the electron microscope (EM).

In the early stages of the development of electron diffraction, experiments were performed by electron diffraction cameras. These cameras were similar in design and function to X-ray diffraction cameras; even today the transmission EM (TEM) is very closely related, in design, to a diffraction camera [3]. However de Broglie's theory also led to the realisation that, if an electron had a wave like nature, it could also be used, like light, for imaging. Furthermore as the resolution that can be obtained in an image is dependent on the wavelength of the illumination, the short wavelength of the electron, when compared to light, makes it possible to resolve much smaller objects using an EM than using a light microscope.

Focussing electrons to produce an image was first demonstrated by Busch [4]
in 1926, who showed that suitably shaped electromagnetic or electrostatic fields could be used as lenses. Then in 1932 Knoll and Ruska [5] published a description of the first electron microscope using electromagnetic lenses, and by 1938 an electron microscope was developed by von Borries and Ruska [6] that was capable of achieving 100Å resolution.

TEM's can display both images and diffraction patterns as shown in fig(1.1). This is very useful when performing structural analyses using electron diffraction, because in many instances the structure that is being inferred from the diffraction pattern can be observed directly in the image. Thus the physical properties of the electron which give electron diffraction its versatility have also led to the development of a sophisticated instrument, the TEM, which performs both electron diffraction and imaging experiments. It is in the TEM that most electron diffraction experiments are currently performed.

Some of the more significant advances in electron diffraction have not come through the refinement of TEM's, but rather through the development of computers and more sophisticated methods of detecting diffraction patterns. In particular there has been a shift away from recording diffraction patterns with photographic emulsion and towards using digital recording instruments, such as charge coupled devices (CCD's) [7] and image plates.

The computer has influenced the development of electron diffraction in a variety of ways. One area where its influence is particularly strong is the use of computers to "control" electron diffraction experiments. Computers connected to the electronics of a TEM can be used to perform experiments automatically or via remote control and allow fine control of the optics of the TEM and the performance of the experiment. Another area where computers have influenced the development of electron diffraction is data processing. Using computers it is possible to extract more information from diffraction patterns than could be achieved previously, through the application of numerical methods to digitised
Figure 1.1: Displays the two basic modes of operation of a TEM. By changing the strength of the intermediate lens the TEM can be used to observe the diffraction pattern formed by the specimen or an image of the specimen.

electron diffraction patterns (new diffraction pattern recording devices have also aided this development, as will be discussed). Computers have also influenced the way electron diffraction data is acquired and stored. It is now possible to record much larger volumes of data in shorter time periods. This data can then be stored electronically and readily accessed at a later date.

Electron diffraction has always had a close association with materials modelling.
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In this area computers have been particularly useful and can now be used to perform, what can be described as "virtual experiments". To perform virtual experiments computers are used to produce model specimens, whose structures are determined by physical laws. These specimens are then used to produce model diffraction patterns and images which give insight into the structure of the real specimen that is being modelled. In this kind of approach to experimentation, agreement between the real experiment and the virtual experiment indicates that there is an element of truth to the physics used to perform the virtual experiment. Computers can also be used to perform virtual experiments that are not possible in reality. In this type of experiment, due care must be taken when interpreting the results but nevertheless useful insight can be gained into the nature of the problem and perhaps its solution.

As mentioned earlier, advances in the methods used to record diffraction patterns have also influenced the development of electron diffraction, in particular the diversity of electron diffraction experiments that can be performed. Digital recording of electron diffraction patterns is now quite common and gives the experimentalist a number of advantages. These include, the ability to process diffraction data as it is being measured, thus divulging important information to the experimentalist whilst the experiment is being performed, greater sensitivity to the detection of electrons than photographic recording and, more importantly for electron diffraction experiments, a much larger dynamic range. Using digital recording techniques it is now possible to measure whole diffraction patterns, without having to make experimental adjustments because of the large intensity distribution in the diffraction pattern. This greatly simplifies diffraction measurements and makes it possible to perform experiments which are not possible using photographic techniques. Digital recording also offers the advantage of a linear intensity scale over the entire dynamic range of the recording device; this allows the data to be readily quantified. Photographic recordings of intensity are non-linear and an electron diffraction pattern recorded in this manner must be
corrected for this non-linearity to obtain quantitative results.

Electron diffraction is now a standard tool being used to perform structural investigations into all sorts of materials. Yet because of its longevity, it is often taken for granted, and new opportunities for obtaining structural information using electron diffraction can be overlooked. However with the new facilities provided by modern technology, redoing old experiments to take advantage of the increased sensitivity and accuracy of experimental apparatus, and performing new experiments designed to make use of and examine the limits to the new technologies, are a particularly fruitful area of research. It is this notion which forms the basic motivation for this thesis.

The subject matter for this thesis is derived from the extension and development of electron diffraction techniques, through the use of new technologies. These techniques are devised specifically for the analysis of amorphous solids, though in some instances they might also be applied to polycrystalline materials. The choice of amorphous materials is because of their importance in optical and electronic devices, as hard coatings and as solar collecting films and also, though there is no direct link, because the production and analysis of electron diffraction patterns from amorphous materials is very similar to that of gases, which was the area that electron diffraction first truly excelled as a tool for structural analysis.

1.2 Electron Diffraction Studies of Amorphous Materials

The question, “What type of material is an amorphous material?”, can be answered simply by stating what an amorphous material is not, “an amorphous material is not crystalline”. However defining what an amorphous material is, has proved to be much more difficult and is a problem that electron diffraction is currently being engaged to solve.
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A simple definition of an amorphous material is a material,

"where the locations of the neighbouring atoms are defined by a probability function such that the probabilities are never unity" [8].

Yet this definition for amorphous materials is only a starting point because in an amorphous material the probability specifying the position of a neighbouring atom on a scale of 0-10Å is reasonably high. That is, amorphous materials exhibit a degree of order on the 0-10Å scale: this order is called short range order (SRO) and is quite clearly observed in the diffraction pattern of an amorphous material, see fig(1.2), which exhibits diffuse but distinct haloes on a steadily falling background.

Electron diffraction has proved to be a very useful tool for quantifying SRO in amorphous materials [9]. Using electron diffraction it is possible to elucidate average SRO structural data in the form of a pair correlation function [10]. Thus electron diffraction has greatly enhanced our knowledge of what an amorphous material is. However the determination of the pair correlation function using electron diffraction only gives a limited description of the structure of an amorphous material as the pair correlation function is a one dimensional average of a three dimensional structure. For this reason, researchers have sought to develop new electron diffraction techniques to obtain a more thorough description of the structure in amorphous materials.

Such a technique proposed by Howie [11] involved measuring intensity correlations from micro-diffraction patterns formed using a scanning transmission electron microscope (STEM). This technique relies on the fact that, through the use of a STEM, very small volumes of an amorphous material can be investigated and as such the averaging involved in more standard electron diffraction techniques can be avoided [12]. It is interesting to note that this technique suggested more than fifteen years ago was a response to the problem of obtaining more information
about the structure of amorphous materials and yet little real progress has been made in this area since that time.

Another approach through which further amorphous structural information has been sought involves the combination of electron diffraction and electron imaging. Electron images of amorphous material provide two dimensional structural information and have been utilised by Howie and Rudee [13, 14] and more recently Gibson and Treacy [15] to obtain structural information from amorphous materials. One problem with these techniques is that, to date, they have only been able to provide qualitative descriptions of the structure in amorphous materials.

In this short discussion of electron diffraction studies of amorphous materials, attention has been focussed on the limitations of current techniques and the measures which are being taken to overcome these limitations. However given the diversity and structural complexity of amorphous materials electron diffraction studies of amorphous materials have been extraordinarily successful. This is evidenced by the wide range of applications that have been developed for amorphous materials. These include computer memory elements, solar cells and optical communications and even though electron diffraction cannot claim to be the sole tool used in the development of these technologies it has played a vital role.

Clearly because of the disordered nature of amorphous materials the complete determination of the structure of an amorphous material is not possible. However a more thorough description of amorphous structure is possible, and it is likely that this information will be afforded by electron diffraction.

1.3 Thesis Outline

In this thesis three diffraction based electron-optical techniques, that can be used to illicit structural information from amorphous materials, are explored. All three techniques are developed for the TEM and are designed to make use of its versatile experimental environment. Thin films of amorphous carbon solids are used almost
Figure 1.2: Electron diffraction pattern measured from a thin film of amorphous carbon with a JEM-2010 FEF and an image plate.

exclusively as samples for analysis, during the testing and development of these techniques, as their well known physical properties aid in the understanding and interpretation of experimental results.

In Chapter 2 a brief review of the theory describing electron diffraction is presented. The theory highlights how the interaction of electron "waves" with the atomic potential within a sample results in the phenomenon of electron diffraction and consequently how an electron diffraction pattern can be used to deduce the structure of that sample. The theory deals specifically with electron diffraction in amorphous materials, but is also applicable to polycrystalline materials. Chapter 2 also outlines the development of a technique by Cockayne and McKenzie [16], which couples a TEM with an electron energy loss spectrometer [17] in order to make particularly sensitive measurements of electron diffraction patterns. Radial distribution function (RDF) analysis is then performed on the elastically scattered component of these measurements to obtain information about the atomic
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structure of the material.

"The calculation of a radial distribution curve is thus the logical first step in the analysis of an electron diffraction photograph" [18].

In Chapter 3 the technique of Cockayne and McKenzie is extended to perform investigations of the electronic structure of amorphous materials. The extension is effected by changing the region of the electron energy loss spectrum that is analysed. Though this is a simple change to make experimentally, the interpretation of the results is more complicated as the electrons being observed are inelastically scattered. The complication arises as, unlike elastically scattered electrons, where the intensity measured in the diffraction pattern is a function of a single variable, momentum \((Q)\), intensity measured for inelastic scattering is a function of two variables momentum and energy \((E)\), and there are a large number of different electron specimen interaction processes through which an electron may lose energy. To investigate the electronic structure of amorphous materials a standard feature in the electron energy loss spectrum, the plasmon, is monitored. This feature exhibits dispersive behaviour which can be measured and used to quantify certain electronic properties of amorphous materials. This technique is also applicable to polycrystalline materials.

Chapter 3 also discusses the implementation of this technique, called plasmon dispersion analysis (PDA), on a TEM, and in particular the automation of the experiment through computer control. As well, this technique is applied to amorphous carbon solids to determine its usefulness as an analytical tool and what direction future development of this technique should take.

Chapter 4 presents a technique which is also an extension of Cockayne and McKenzie's original (RDF) technique. One advantage of using electron diffraction is its ability to investigate small volumes of material (as has been mentioned previously). This advantage can be extended through the focussing of the elec-
tron beam. However when focussing electrons to investigate very small volumes of materials, the electron optics results in convergent illumination. This creates an obstacle to the performance of RDF analysis which requires that parallel electron illumination be used. To overcome this problem, and take advantage of the very small volumes that can be illuminated through focussing of the electron beam, an assumption is made that the diffraction patterns formed for each of the different directions of incidence of the convergent illumination are identical. This allows the diffraction pattern formed with convergent illumination to be considered as a convolution of the diffraction patterns from all the different directions of the incident beam. The technique presented in this Chapter involves the deconvolution of electron diffraction data, using modern numerical methods, including maximum entropy (ME) and iterative blind deconvolution (IBD). This Chapter explores the new avenues for research that are now available through the combination of digital recording of electron diffraction data and numerical methods.

Chapter 5 introduces a technique that also aims to deduce structural information from amorphous materials. This technique, based on work done by Gibson and Treacy [15], is exclusive in its application to amorphous materials and utilises dark field images of amorphous materials. The structure in amorphous materials can be described by correlation functions; RDF analysis reveals information about two particle correlations within the materials. However often this information is not sufficient to distinguish between amorphous materials that have only subtle structural differences. The technique addresses this problem by measuring features in dark field images that are dependent upon higher order correlation functions. The technique is simulated using models of amorphous materials, developed using ab initio quantum mechanical methods and the high resolution TEM (HRTEM) simulation package of Cerius 2.1. From these simulations it is possible to establish what conditions are required to perform this experiment in a TEM.

Chapter 6 contains a discussion of the strengths and weaknesses of these tech-
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niques as well as suggestions for furthering their development and application.
References Chapter 1


CHAPTER 2

Elastic Scattering: Theory and Experiment

The structure of amorphous and polycrystalline materials can be investigated by collecting scattering data to large scattering angles, and converting the data into information about atomic spatial relationships. The scattering data can be obtained using either electrons, neutrons or X-rays; however when investigating thin films only electrons can be used due to the small scattering cross sections of neutrons and X-rays.

A convenient environment for performing electron scattering experiments is provided by the modern transmission electron microscope (TEM). With standard acceleration voltages between 100kV and 400kV, the TEM allows fine control over a beam of high energy electrons enabling sophisticated diffraction experiments
Chapter 2: Elastic Scattering: Theory and Experiment

to be performed. A further advantage of the TEM is the very short specimen change over time, which makes it possible to examine a number of different specimens in only a few hours. More recently the TEM has been coupled to a variety of different spectrometers. These include the X-ray energy dispersive spectrometer (XEDS) [1] and the electron energy loss spectrometer (EELS) [2, 3]. This has increased the amount of information that can be ascertained about a material in a TEM and has extended the range of possible applications for the TEM.

The quality of the experimental environment provided by the TEM makes gathering and analysing electron scattering data relatively simple. This can lead to a false sense of accomplishment in the experimentalist as the interpretation of this data requires a thorough understanding of how a high energy electron beam interacts with a material. The problem of interpretation is further compounded by the fact that the electron can interact with a material in a variety of different ways, producing a number of different detectable signals. These signals include backscattered electrons, Auger electrons and elastic and inelastically scattered electrons. Of all the possible interactions, it is through the measurement of elastically scattered electrons that the atomic structure of a material can most readily be determined. Though it will be explained later in more detail, the primary mechanism for the elastic scattering of electrons is the Coulombic interaction between the electron and the atom.

By definition an elastic scattering event is a collision in which kinetic energy is conserved [4]. When an electron is elastically scattered by an atom, the large difference between the masses of the particles means that the electron may suffer a change in momentum but that its kinetic energy will be conserved. As a consequence of the fact that electrons have a wave-like nature, as postulated by de Broglie in 1925 [5], electrons that are elastically scattered exhibit coherency. Coherency is a term used to describe how the phases of different electron waves relate. If, for example, there is a constant phase relationship between two waves they are described as being completely coherent. Alternatively if there is no phase
relationship between two waves they are described as being incoherent. It is also possible for two waves to have a partial phase relationship; in this situation the waves exhibit a degree of coherence which lies in between that of complete coherence and incoherence. For elastically scattered electrons the degree of coherence decreases as the scattering angle increases. In the TEM low angle elastic scattering (i.e. angles less than \( \approx 4^\circ \)) is highly coherent and gives rise to diffraction phenomena which can be used to obtain structural information about a material.

In the first part of this Chapter the theory describing the single elastic scattering of an electron by an atom and an assembly of atoms is reviewed. This theory is then developed for the specific case of single elastic scattering by an amorphous material containing a single atomic species. After that, the developed theory is extended to include single elastic scattering by an amorphous material containing multiple atomic species. Finally multiple scattering in amorphous materials is discussed. In this first Section all of the theory is presented from the perspective of the wave-like nature of an electron to enable the understanding of electron diffraction effects.

In the second part of this Chapter an experimental technique for measuring energy filtered electron diffraction patterns (EFDP) with a TEM is reviewed; the technique assumes that the experimental conditions required to obtain single elastic scattering have been satisfied. Even though both the theory and the EFDP technique presented are well documented [6, 7, 8, 9], the work presented in later Chapters relies heavily on the process of elastic scattering by amorphous materials and the extension and application of the EFDP technique, so this information is included here.

2.1 Theory

The scattering of an electron by an atom is a time dependent process. At a time \( t_1 \) the electron is far away from the atom, and there is no interaction between them.
At time $t_2$ the electron and atom are close enough to interact and the electron is scattered by the atom. Finally at time $t_3$ the electron and atom are again sufficiently far enough apart that there is no interaction between them. Although this time dependent process is easy to conceptualise, using quantum mechanics the scattering process can be reformulated as a stationary state problem and can be considered to be time independent [10]. The time independent Schrödinger equation (TISE) is then solved to determine the wavefunction $\Psi(r)$ that describes the position and energy of the electron. In the following derivation of $\Psi(r)$, individual components of $\Psi(r)$ are referred to as the state of the electron before and after scattering. This makes the derivation more intuitive, but referring to the components of $\Psi(r)$ in this way is not strictly correct as the scattering process is being treated independently of time.

### 2.1.1 Scattering from a Single Atom

Consider the scattering of a single electron by an atom, where the electron is described by a matter wave, normally called a wave function and expressed as $\Psi(r, t)$. The wavefunction is a probability amplitude and $|\Psi(r, t)|^2$ gives the probability density for finding a particle or assembly of particles at a position $r$ within a certain time $\Delta t$ or within a volume $\Delta r$ at a time $t$ [11]. As previously mentioned the electron interacts through Coulombic forces with the electrostatic potential of the atom, $V(r, t)$. This interaction between the electron and the atom can be described by the Schrödinger wave equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r, t) \Psi(r, t) = -i\hbar \frac{d}{dt} \Psi(r, t),$$

(2.1)

where $\hbar$ is Planck’s constant divided by $2\pi$, $m$ is the mass of the electron and $\nabla$ is the Laplacian differential operator.

If the time variation of $V(r, t)$ is slow when compared to $\Psi(r, t)$, it may be assumed that the electrostatic potential is time independent and that $V(r, t) \approx$...
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\( V(\mathbf{r}) \). It may also be assumed that \( \Psi(\mathbf{r}, t) \) is separable, that is,

\[
\Psi(\mathbf{r}, t) = \Psi(\mathbf{r}) e^{-iEt/\hbar},
\]

where \( E \) is the energy of the electron. Then substituting these quantities into the Schrödinger equation, eqn(2.1), gives the TISE

\[
\left[ \nabla^2 + \frac{2m}{\hbar^2} (E - V(\mathbf{r})) \right] \Psi(\mathbf{r}) = 0. \tag{2.3}
\]

The derivation of the solution to the TISE for the scattering of an electron by an atom can be simplified by considering the solutions to the TISE at positions \( \mathbf{r} \), before and after the scattering event, separately. The solution to the TISE at positions \( \mathbf{r} \) before the scattering event can be thought of as describing the incident electron, \( \Psi_{\text{inc}}(\mathbf{r}) \), and after the scattering event as describing the scattered electron, \( \Psi_{\text{scatt}}(\mathbf{r}) \). These solutions can then be combined to give the solution to the TISE for the scattering of an electron by an atom, \( \Psi(\mathbf{r}) \).

Before the scattering event the electron is moving in free space \( (V(\mathbf{r}) = 0) \) and the TISE can be written as

\[
\left[ \nabla^2 + \frac{2m}{\hbar^2} E \right] \Psi_{\text{inc}}(\mathbf{r}) = 0. \tag{2.4}
\]

Solving this equation for \( \Psi_{\text{inc}}(\mathbf{r}) \) gives

\[
\Psi_{\text{inc}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}. \tag{2.5}
\]

Eqn(2.5) describes a plane wave of unit amplitude and wave vector \( \mathbf{k} \), where \( |\mathbf{k}| = \frac{2\pi}{\lambda} \) (\( \lambda \) is the wavelength of the electron).

After the scattering event, to a distant observer, the atom appears to be an electron wave source, emitting electron waves into free space. Once again \( V(\mathbf{r}) = 0 \), and the TISE is written as,

\[
\left[ \nabla^2 + \frac{2m}{\hbar^2} E \right] \Psi_{\text{scatt}}(\mathbf{r}) = \rho(\mathbf{r}). \tag{2.6}
\]

In eqn(2.6) \( \rho(\mathbf{r}) \) represents the electron wave source.
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The solution to eqn(2.6) can be obtained by assuming, for the moment, that the electron wave source is a point source, consequently \( \rho(r) \) may be represented by a delta function (i.e \( \rho(r) = B \delta(r-r') \), where \( B \) is the strength of the source). Using this assumption, the solution to the TISE is

\[
\Psi_{sph}(r) = \left( \frac{B}{4\pi} \right) \frac{e^{ik'r - r'}}{|r-r'|}.
\]  

(2.7)

Eqn(2.7) is a spherical wave centred on the source which decreases in amplitude as the radial distance from the source \(|r-r'| \) increases.

Now, it is assumed that the atomic potential, \( V(r) \), can be represented by a finite distribution of point sources and that the strength of each point source is given by the interaction of \( V(r) \) and \( \Psi(r) \), that is \( B = B(r) = V(r)\Psi(r) \). In this case \( \Psi_{scatt}(r) \) is then the superposition of the spherical waves, \( \Psi_{sph}(r) \), scattered from each of the individual point sources.

\[
\Psi(r)_{scatt} = \frac{1}{4\pi} \int_0^\infty V(r')\Psi(r') \frac{e^{ik'|r-r'|}}{|r-r'|} dr'.
\]  

(2.8)

In fig(2.1) \( \Psi(r) \), the wavefunction describing the scattering of an electron by an atom, is depicted as having two components \( \Psi_{inc}(r) \) and \( \Psi_{scatt}(r) \). Recalling that \( \Psi(r) \) is time independent and describes the position and energy of the electron before, during and after scattering, it can be stated that \( \Psi(r) = \Psi_{inc}(r) + \Psi_{scatt}(r) \). Then combining the solutions for \( \Psi_{inc}(r) \) and \( \Psi_{scatt}(r) \) into an expression for \( \Psi(r) \) gives

\[
\Psi(r) = e^{ikr} + \frac{1}{4\pi} \int_0^\infty V(r')\Psi(r') \frac{e^{ik'|r-r'|}}{|r-r'|} dr'.
\]  

(2.9)

The difficulty with solving the integral in eqn(2.9) to obtain the form of \( \Psi(r) \) is that the integration is itself dependent on the solution through the interaction of \( \Psi(r) \) and \( V(r) \). However under the condition that the amplitude of the scattered wave is much smaller than that of the incident wave it may be assumed that \( \Psi(r) \) in the integral of eqn(2.9) can be replaced with \( \Psi_{inc}(r) \), the incident component of the electron wave. This approximation is known as the Born approximation
\[ \psi(r) = \psi_{inc}(r) + \psi_{scatt}(r) \]

\[ \cdot = \text{point source} \]

**Figure 2.1:** Diagram showing the scattering of a planar electron wave by an atom. The potential \( V(r) \) is assumed to be made up of a finite distribution of point sources of strength \( B(r) = V(r) \psi(r) \).

of the first order and, in the case of an electron beam being scattered through a material, is equivalent to assuming that each electron is only scattered once, a situation known as kinematic scattering. Employing the Born approximation, eqn(2.9) becomes

\[ \psi(r) = e^{ik_r} + \frac{1}{4\pi} \int_0^{\infty} V(r') \psi_{inc}(r') e^{i k'_r |r-r'|} dr'. \]  

(2.10)

Furthermore, at large distances from the scattering centre where measurements of \( |\psi(r)|^2 \) are normally made, eqn(2.10) may be simplified by recognising that, since \( r >> r' \),

\[ \frac{e^{i k'_r |r-r'|}}{|r-r'|} \approx \frac{e^{i k'_r r}}{r} \cdot e^{-ik_r r'}, \]

and eqn(2.9) becomes

\[ \psi(r) = e^{ik_r} + \frac{1}{4\pi} \frac{e^{i k'_r r}}{r} \int_0^{\infty} V(r') \psi_{inc}(r') e^{-ik_r r'} dr'. \]  

(2.11)

Using eqn(2.5) and making the substitution \( Q = k - k' \), the integral in eqn(2.11)
can be written as
\[ f(Q) = \int_0^\infty V(r') e^{iQr'} dr', \quad (2.12) \]
where \( Q = |Q| \) and \( f(Q) \) is the atomic scattering factor. \( f(Q) \) is an important quantity in the study of diffraction for a number of reasons. \( f(Q) \) describes the angular dependence and amplitude of the scattered wave and \( |f(Q)|^2 \) is proportional to the scattered intensity. From eqn(2.12) it can be seen that \( f(Q) \) is the Fourier transform of the atomic potential, thus demonstrating the direct relationship between the intensity of elastically scattered electrons and the atomic potential. It is important to note that whilst the Born approximation is reasonable for light atoms, it is not justified for heavy atoms. Thus the use of the Born approximation to determine \( f(Q) \) for heavy atoms will introduce error into the estimate of \( f(Q) \). Despite this \( f(Q) \) values (in particular platinum \( f(Q) \) values) determined using the first Born approximation will be used in Section 2.4 of this Chapter. This is because the effect that the error has on the final result of the analysis is minimal.

### 2.1.2 Scattering from an Assembly of Atoms

An assembly of atoms can be described by an array of \( N \) atoms at positions \( r_m \). The scattering amplitude from an assembly of atoms, \( F(Q) \), called the structure factor can be derived by recognising that \( F(Q) \) is the Fourier transform of the atomic potential of the assembly of atoms [12]. The atomic potential for the assembly of atoms is given by
\[ V(r) = \sum_{m=1}^N V_m(r - r_m). \quad (2.13) \]
Substituting this potential into eqn(2.12) gives
\[
F(Q) = \sum_{m=1}^N \int_0^\infty V_m(r - r_m) e^{iQr} dr
= \sum_{m=1}^N \int_0^\infty V_m(r') e^{iQr'} e^{iQr_m} dr'
= \sum_{m=1}^N f_m(Q) e^{iQr_m}. \quad (2.14)
\]
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Using the relationship that \(|F(Q)|^2\) is proportional to the scattered intensity from an assembly of atoms, the diffraction pattern can now be described mathematically as

\[
I(Q) = \sum_{m=1}^{N} \sum_{n=1}^{N} f_m(Q)f_n(Q)e^{iQ \cdot r_{mn}},
\]

(2.15)

where \(r_{mn} = r_m - r_n\). From eqn(2.15) it can be seen that the scattered intensity \(I(Q)\) is dependent on the atom type through the atomic scattering factors and the distance separating atom pairs at positions \(r_m\) and \(r_n\). Hence the diffracted intensity is dependent on the structure of the material through \(r_{mn}\).

2.1.3 Obtaining Structural Information from Diffraction Data

In Section 2.1.2 a mathematical description of the diffraction pattern, \(I(Q)\), formed from an assembly of atoms was developed. In this Section \(I(Q)\), which would normally be obtained experimentally, is Fourier transformed to obtain information about the atomic structure within the sample from which the diffraction pattern was formed. It is assumed that the sample is taken from an amorphous material.

2.1.3.1 Single Atomic Species

If the sample contains a single atomic species a number of modifications can be made to eqn(2.15). Clearly \(f_m(Q)\) will equal \(f_n(Q)\) and the subscripts on the atomic scattering factors may be dropped. Also the double summation of eqn(2.15) may be split into self and cross terms, self terms occurring when \(n = m\) and cross terms when \(n \neq m\). Eqn(2.15) can then be written as

\[
I(Q) = \sum_{m=1}^{N} f(Q)^2 + \sum_{m=1}^{N} f(Q)^2 \sum_{n \neq m} e^{iQ \cdot r_{mn}}.
\]

(2.16)

Following Warren [13] a density function \(p_m(r_{mn})\) is introduced, where \(p_m(r_{mn})dV_n\) is the number of atoms in a volume element \(dV_n\), and is used to replace the summation over \(n \neq m\) with an integral. Essentially the summation
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over atom positions in eqn(2.13) is being replaced by a continuous function which defines the atomic locations.

\[ I(Q) = N f(Q)^2 + \sum_m f(Q)^2 \int_B p_m(r_{mn}) e^{iQ \cdot r_{mn}} dV_n. \]  

(2.17)

In eqn(2.17) \( B \) specifies the volume of the sample.

The average density of the sample, \( p_{avg} \), is then added and subtracted from eqn(2.17) to obtain

\[ I(Q) = N f(Q)^2 + \sum_m f(Q)^2 \int_B (p_m(r_{mn}) - p_{avg}) e^{iQ \cdot r_{mn}} dV_n \]

\[ + \sum_m f(Q)^2 \int_B p_{avg} e^{iQ \cdot r_{mn}} dV_n. \]  

(2.18)

The third term in eqn(2.18) is dependent upon the shape of the specimen and is only significant for very small scattering angles. Representing the third term by \( S(Q) \), it can be shown [13] that, for a spherical specimen of radius \( R \),

\[ S(Q) = 9 \left[ \frac{\sin(QR) - QR\cos(QR)}{(QR)^3} \right]^2. \]  

(2.19)

To quantify the magnitude of the contribution that \( S(Q) \) makes to \( I(Q) \), calculations of \( S(Q) \) and \( I(Q) \) were made using eqn(2.15) and eqn(2.19) respectively. \( I(Q) \) was calculated from a model of amorphous silicon, prepared by Nick Cooper using Car-Parrinello molecular dynamics (CPMD) [14]. The model contains 64 silicon atoms in a cube which has a side length of 10.86Å. \( S(Q) \) was evaluated for a value of \( R \) which was equal to the distance from the centre to a corner of the cube of amorphous silicon. The results of these calculations are shown in fig(2.2).

By comparing the magnitude of \( S(Q) \) and \( I(Q) \), in fig(2.2) it can be seen that \( S(Q) \) makes a negligible contribution to \( I(Q) \), and can be ignored. Alternatively as \( S(Q) \) is only dependent on \( p_{avg} \), \( S(Q) \) can be evaluated and subtracted from \( I(Q) \).

If it is assumed that \( S(Q) \) has been evaluated and subtracted from \( I(Q) \), eqn(2.18)
Figure 2.2: A comparison of $I(Q)$ and $S(Q)$ calculated from a model of amorphous silicon. Notice that $S(Q)$ makes a negligible contribution to $I(Q)$.

becomes

$$I(Q) = N f(Q)^2 + \sum_{m} f(Q)^2 \int_{B} (p_{m}(r_{mn}) - p_{avg}) e^{iQ \cdot r_{mn}} dV_n.$$ (2.20)

Next $p_{m}(r_{mn})$ is replaced by $p(r) = < p_{m}(r_{nm}) >$ where the average is determined for all atoms $m$ within the sample. As a consequence of the homogenous property of amorphous materials $p(r) - p_{avg}$ is the same for whichever atom $m$ the integral in eqn(2.20) is performed over, and thus the summation over $m$ can be replaced by $N$, the total number of atoms in the sample. Also because amorphous materials are isotropic, $r$ can be replaced by $r = |r|$. Eqn(2.20) is then

$$I(Q) = N f(Q)^2 + N f(Q)^2 \int_{B} (p(r) - p_{avg}) e^{iQ \cdot r} dV_n.$$ (2.21)

Transforming to spherical coordinates, and performing the integration in
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eqn(2.21) over the angular components, gives

\[ I(Q) = N f(Q)^2 + N f(Q)^2 \int_0^\infty (p(r) - p_{avg}) \frac{\sin(Qr)}{Qr} 4\pi r^2 dr. \quad (2.22) \]

This equation may be rearranged such that the experimentally observable terms are on the left hand side and the information about atomic structure is on the right hand side.

\[ Q \left[ \frac{I(Q) - N f^2(Q)}{N f^2(Q)} \right] = 4\pi \int_0^\infty r (p(r) - p_{avg}) \sin(Qr) dr. \quad (2.23) \]

By defining a function \( \Phi(Q) \),

\[ \Phi(Q) = Q \left[ \frac{I(Q) - N f^2(Q)}{N f^2(Q)} \right], \quad (2.24) \]

it becomes apparent that the function \( \Phi(Q) \) is the Fourier sine transform of \( 4\pi r (p(r) - p_{avg}) \), which is the reduced density function, \( G(r) \).

\[ G(r) = \frac{2}{\pi} \int_0^\infty \Phi(Q) \sin(Qr) dQ. \quad (2.25) \]

\( G(r) \) is readily obtainable from the experimentally measured diffraction intensity and is a useful function because the positions of the peaks in \( G(r) \) correspond to nearest neighbour distances within the sample. Also, the relationship between \( G(r) \) and \( p(r) \) allows \( G(r) \) to be integrated to determine coordination numbers.

\[ C(r_1, r_2) = \int_{r_1}^{r_2} 4\pi r^2 p(r) dr = \int_{r_1}^{r_2} r (G(r) - p_{avg}) dr, \quad (2.26) \]

where \( C(r_1, r_2) \) is the number of atoms between the radial distances \( r_1 \) and \( r_2 \) from an atom \( m \).

2.1.3.2 Multiple Atomic Species

For materials with more than one atomic species it is possible to develop an approximate method for inversion of eqn(2.15), through the use of chemically averaged atomic scattering factors [15]. If the number of atoms of type \( i \) in the
specimen is represented by $U_i$ and the number of different types of atom in the specimen is represented by $U$, then the chemically averaged atomic scattering factor is defined as,

$$ < f(Q) > = \frac{1}{N} \sum_{i=1}^{U} U_i f_i(Q), \quad (2.27) $$

and the mean of the square of the chemically averaged atomic scattering factor is defined as,

$$ < f^2(Q) > = \frac{1}{N} \sum_{i=1}^{U} U_i f_i^2(Q), \quad (2.28) $$

where $N = \sum_{i=1}^{U} U_i$ in both eqn(2.27) and eqn(2.28).

Furthermore if it is assumed that the atomic scattering factor for a particular atomic species is equal to the number of electrons, $T_m$, of the species multiplied by the chemically averaged atomic scattering factor, which is equivalent to assuming that the atomic scattering factors of the different species are proportional to one another, that is

$$ f_m(Q) = T_m < f(Q) >, \quad (2.29) $$

then eqn(2.15) can be written as,

$$ I(Q) = N < f^2(Q) > + < f(Q) >^2 \sum_{m} T_m \sum_{n \neq m} T_n e^{iQ \cdot r_{nm}}. \quad (2.30) $$

The summation over $n \neq m$ may be split by considering a particular atom $m$ and identifying the different types of neighbouring atoms $i$. This gives

$$ I(Q) = N < f^2(Q) > + < f(Q) >^2 \sum_{m} T_m \sum_{i=1}^{B_i} \sum_{j=1}^{B_i} T_{ij} e^{iQ \cdot r_{(ij)m}}, \quad (2.31) $$

where the index pair $(ij) \equiv n \neq m$.

If $p_{mi}(r_{(ij)m}) dV_{(ij)}$ is defined as the number of atoms of type $i$ at a distance $r_{(ij)m}$ from the atom $m$ in a volume element $dV_{(ij)}$, the summation over $j$ can be

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replaced by an integral over the volume of the sample \( B \).

\[
I(Q) = N < f^2(Q) > + \\
< f(Q) >^2 \sum_m T_m \sum_{i=1}^U T_i \int_B p_{mi}(r_{(ij)m}) e^{iQ \cdot r_{(ij)m}} dV_{(ij)}. \tag{2.32}
\]

Addition and subtraction of \( p_{avg_i} \), the density of atoms of type \( i \) within the sample, from eqn(2.32), gives

\[
I(Q) = N < f^2(Q) > + \\
< f(Q) >^2 \sum_m T_m \sum_{i=1}^U T_i \int_B [p_{mi}(r_{(ij)m}) - p_{avg_i}] e^{iQ \cdot r_{(ij)m}} dV_{(ij)}, \tag{2.33}
\]

where it has been assumed that the small angle scattering term has been subtracted off.

By considering the atom type \( l \) in the summation over \( m \) and setting

\[ p_{li}(r) =< p_{mi}(r_{(ij)m}) >_m \], which is the average over all the atoms \( m \) of type \( l \), eqn(2.33) becomes

\[
I(Q) = N < f^2(Q) > + \\
< f(Q) >^2 \sum_l U_l T_l \sum_{i=1}^U T_i \int_B [p_{li}(r) - p_{avg_i}] e^{iQ \cdot r} dV. \tag{2.34}
\]

Performing the integration in eqn(2.34) over the angular components of a spherical coordinate system and noting that \( r \) can be replaced by \( r = |r| \) for an isotropic assembly of atoms gives

\[
I(Q) = N < f^2(Q) > + \\
< f(Q) >^2 \sum_l U_l T_l \sum_{i=1}^U T_i \int_0^\infty [p_{li}(r) - p_{avg_i}] \frac{\sin(Qr)}{Qr} 4\pi r^2 dr. \tag{2.35}
\]

Then by defining

\[
p(r) = \frac{1}{N} \sum_{l=1}^U \sum_{i=1}^U U_l T_l T_i p_{li}(r), \tag{2.36}
\]

and recognising that

\[
\sum_{l=1}^U \sum_{i=1}^U U_l T_l T_i p_{avg_i} = N p_{avg}, \tag{2.37}
\]
where $p_{\text{avg}}$ is the average density of the specimen when all atomic species are included. Eqn(2.35) can then be written as

$$I(Q) = N < f^2(Q) > + N < f(Q) >^2 \int_0^\infty [p(r) - p_{\text{avg}}] \frac{\sin(Qr)}{Qr} 4\pi r^2 dr.$$  

(2.38)

Eqn(2.38) is analogous to eqn(2.22) and can be converted to $G(r)$ in a similar fashion. However in this case $G(r)$ is a combination of all the partial radial distribution functions from each of the atomic species and as such care must be taken when interpreting $G(r)$.

2.1.4 Multiple Elastic Scattering

In the theory developed so far it has been assumed that an electron, upon entering a specimen, will only be scattered once before it exits the specimen. As previously mentioned this assumption is known as the "single scattering" or "kinematical" approximation [16] and was applied in eqn(2.10) where it was assumed that the amplitude of the scattered electrons, $\Psi_{\text{scatt}}(r)$, was very small when compared with the amplitude of the incident electrons, $\Psi_{\text{inc}}(r)$.

The assumption of single scattering is based on the relationship between $Z$, the thickness of the specimen, and $\lambda_e$ the mean free path for elastic scattering where the mean free path for elastic scattering is the average distance that an electron travels between elastic scattering events [17]. Clearly the probability for multiple scattering increases as the ratio $\frac{Z}{\lambda_e}$ increases.

A short theoretical treatment of multiple elastic scattering in disordered materials has been developed by Anstis [18] and is followed here to facilitate understanding of multiple scattering effects in amorphous materials. Anstis begins with the phase grating approximation [16]:

$$\Psi(x, y) = e^{i\sigma \phi(x, y)Z},$$  

(2.39)

where $\phi(x, y)$ is the electrostatic potential within the specimen projected onto
the \( x, y \) plane and \( \sigma = \frac{\pi}{AE} \) is the interaction constant, where \( \lambda \) is the wavelength of the electron and \( E \) is the electron's kinetic energy.

Fourier transformation of \( \Psi(x, y) \) gives \( \Psi(Q) \),

\[
\Psi(Q) = \int dx \int dy \ e^{iQx}\Psi(x, y).
\]  

Note that as the diffraction pattern is circularly symmetric only a single reciprocal space coordinate \( Q \) is required and the Fourier transform can be effected using only one real space coordinate, either \( x \) or \( y \). From \( \Psi(Q) \), the intensity in the diffraction pattern \( I(Q) \) can be determined through the relationship \( I(Q) = |\Psi(Q)|^2 \). The result obtained for \( I(Q) \) through expansion of the exponential term in eqn(2.39) is

\[
I(Q) = \left[ \delta(Q) + ZI_{\text{single}}(Q) + \frac{1}{2!}Z^2I_{\text{single}}(Q) \ast I_{\text{single}}(Q) + \ldots \right] e^{-\frac{Q^2}{4}},
\]  

where \( \ast \) indicates that a convolution is to be performed and \( I_{\text{single}}(Q) \) is the single scattering distribution which is equivalent to \( I(Q) \) in eqn(2.15). The delta function, \( \delta(Q) \), represents the unscattered electrons, and the successive terms involving \( I_{\text{single}}(Q) \) represent the contribution of single scattering, double scattering etc, to the intensity in the diffraction pattern. The exponential term in eqn(2.41) attenuates the intensity observed in the diffraction pattern.

From eqn(2.41) it can be seen that the multiply scattered terms are self convolutions of the single scattering distribution and that as \( Z \) increases the proportion of the observed spectrum derived from the multiply scattered terms increases due to their dependence on higher powers of \( Z \).

Eqn(2.41) can be simplified by Fourier-Bessel transformation, in which case

\[
I(r) = 2\pi \int_0^\infty Q J_0(Qr)I(Q)dQ = I_0e^{Z(I_{\text{single}}(r) - \frac{1}{2})}.
\]  

It is then possible to obtain the single scattering distribution \( I_{\text{single}}(r) \) by taking
the natural logarithm of both sides of eqn(2.42).

\[ I_{\text{single}}(r) = \frac{1}{Z} \ln \left[ \frac{I(r)}{I_0} \right] + \frac{1}{\lambda}. \] (2.43)

Hence, because of the independent nature of multiple scattering in amorphous materials, it is possible to recover the single scattering intensity distribution from the multiply scattered intensity distribution using Fourier-log deconvolution techniques. Thus it is possible to perform \( G(r) \) analysis on specimens that are too thick to satisfy the kinematical approximation.

### 2.1.5 Conclusion-Elastic Scattering Theory

Through the development of the theory of elastic scattering of electrons by amorphous materials it has been shown how it is possible to obtain structural information from a specimen. In summary, electrons are elastically scattered from atomic potentials and the scattered electrons form a diffraction pattern which is experimentally measurable. The data measured is then manipulated to obtain structural information about the sample. It is this process which forms the basis of the experimental technique described in the following Sections.

### 2.2 Energy Filtered Electron Diffraction

A selected area diffraction (SAD) pattern formed in a TEM, under experimental conditions that satisfy the criteria for kinematic scattering, is comprised of both elastic and inelastically scattered electrons. However the theory developed in Section 2.1.2. describing the scattering of electrons by an assembly of atoms assumed that the scattered electron underwent an elastic collision with the atom. Therefore utilisation of diffraction data comprising of both elastic and inelastically scattered electrons does not satisfy the theoretical criterion for elastic scattering. To overcome this problem an experimental technique is needed to separate the intensity in the diffraction pattern into its elastic and inelastic components. Structural analysis can then be performed from the elastically scattered
data which complies with the theoretical assumption.

A technique that allows the diffraction pattern formed in a TEM to be separated into its elastic and inelastic components was developed by Cockayne and McKenzie [8, 19, 20]. The separation was achieved by the coupling of a TEM to an electron energy loss spectrometer (EELS). A diffraction pattern formed from only elastically scattered electrons was then obtained and called an energy filtered diffraction pattern (EFDP) because the inelastic contribution to the diffraction pattern had been “filtered” out.

2.2.1 Overview of the Technique

The technique of Cockayne and McKenzie is designed to allow structural analysis of both polycrystalline and amorphous materials in very short periods of time and has been successfully applied to a wide range of problems [21, 22, 23, 24]. As initially introduced, a conventional TEM (CTEM) (Philips 430) operating at 300kV, employing parallel electron illumination, is used to form a selected area diffraction pattern. The diffraction pattern is then projected onto the entrance aperture of an energy loss spectrometer. Originally this was a GATAN serial EELS (SEELS) but this has since been replaced by a GATAN 666 parallel EELS (PEELS). The spectrometer itself is fitted to the base of the column of the TEM. The PEELS is then used to collect an energy loss spectrum from the electrons accepted by its entrance aperture. Finally a measurement of the intensity in a finite region of this energy loss spectrum, centered on $E = 0$, is made. This allows the elastically scattered component of the diffraction pattern at a point $Q$ to be determined. A schematic outline of the setup is shown in fig(2.3).

To obtain the elastic scattering contribution at each position $Q$ in the diffraction pattern, the diffraction pattern is scanned across the entrance aperture to the PEELS. The scanning is performed by a digitally incremented signal applied to the post specimen scan coils. The signal is formed by the ramp generator of a Serial EELS (SEELS) unit and applied to the scan coils through the hybrid
diffraction unit of the EM430. The scan coils are placed near the back focal plane of the objective lens and the choice to use post specimen deflection as opposed to tilting the incident beam was made due to the difficulty in maintaining a constant volume of illumination over a large range of tilt angles [8].

The complete process of scanning the diffraction pattern and collection of electron energy loss spectra is performed by GATAN EL/p software supplemented by a purpose built 'Custom function' that allows the EL/p program to be used as a multichannel analyser (MCA) for data collection and analysis.
2.2.2 PEELS

Of fundamental importance to the whole technique is the use of the PEELS to separate the diffraction pattern into its elastic and inelastic components. In the technique the PEELS is used to measure the energy of a finite distribution of electrons scattered to positions \( Q \pm \frac{1}{2} \Delta Q \) within the diffraction pattern, where \( \Delta Q \) is defined by the size of the entrance aperture to the PEELS, and \( Q \) is defined by the position of the diffraction pattern with respect to the position of the entrance aperture of the PEELS.

The PEELS measures the energy of the electrons selected by its entrance aperture by passing them through a magnetic field which causes the electrons to travel along curved trajectories of different radii depending upon their kinetic energy. The relationship between the kinetic energy of the electron and the radius of the curved trajectory is expressed mathematically as

\[
R = \frac{\gamma}{eB}(2m_0E)^{\frac{1}{2}},
\]

where \( R \) is the radius of the curved trajectory, \( \gamma \) is a relativistic correction, \( m_0 \) is the rest mass of the electron, \( e \) is the charge on the electron, \( B \) is the magnetic field strength and \( E \) is the kinetic energy of the electron.

Having separated the electrons spatially according to their energy, a detector is employed to measure the intensity of the electrons as a function of their energy; forming an "energy loss spectrum". The period of time over which the measurement is made is called the "integration time".

There are a number of important features to note in an electron energy loss spectrum, fig(2.4). The large spike corresponding in position to no energy loss, called the zero loss peak (ZLP), is formed from elastically scattered electrons. The broad peak adjacent to the ZLP, called the plasmon peak, is formed from electrons which have lost energy in a process causing a quantised longitudinal oscillation of the valence electron density. Broadly speaking the ZLP is comprised
Figure 2.4: Electron energy loss spectrum, displaying both the zero loss peak and the plasmon peak.

of elastically scattered electrons and all other features in the energy loss spectrum are comprised of inelastically scattered electrons, with thermal diffuse scattering being regarded, in this instance, as a form of inelastic scattering [25].

2.2.3 The PEELS Detector

Integration of the ZLP in the energy loss spectrum allows the elastically scattered electrons at a position $Q \pm \frac{1}{2} \Delta Q$ to be determined. However a number of artefacts are introduced into the energy loss spectrum by the intrinsic properties of the PEELS detector and these artefacts will introduce error into the measurement of the elastic component of the diffraction pattern if they are not overcome.

The PEELS detector is formed by the optical coupling of a YAG scintillator crystal to a Hamamatsu S2304 – 1024F 1024 element array of silicon diodes, fig(2.5). Each element is approximately 25µm high and 2.5mm wide [26] and has a dynamic range of less than $10^5$. The system works quite simply:- before a measurement is taken the silicon diodes are charged. Then, during a measure-
Figure 2.5: A schematic diagram of the PEELS. The YAG is optically coupled to the photo-diode array.

ment, electrons admitted to the spectrometer through its entrance aperture strike the scintillator crystal producing photons. The photons in turn strike the silicon diodes depleting the stored charge as they do so. After the integration period is completed the remaining charge is read serially from the photo-diode array and recorded digitally.

There are two main problems encountered when using this type of detection system. One problem is the non-uniform response of the photo-diode array, which is due to gain variations between the individual diodes. The other problem arises as a consequence of the incomplete recharging of the diodes after a measurement. This causes spurious charge to be present in subsequent measurements and is often referred to as a “memory effect”. Both of these problems introduce error
into intensity measurements.

Management of the diode-to-diode gain variation is currently achieved by consistently taking measurements from the same region on the photo-diode array. This method does not eliminate gain variation, it simply ensures that its contribution is the same to each spectrum and as such can be quantified and removed. Maintaining the position of the spectrum on the photo-diode array is difficult because the spectrum tends to drift with time due to the drift of the high tension supply with respect to the spectrometer. Correction for the drifting of the spectrum is achieved by defining a 40 channel “window” (where each channel corresponds to a single silicon diode and an energy range of 0.2eV) around the initial position of the ZLP, which is itself 10-15 channels wide. Then the position of the ZLP, within the window, can be determined using a peak search algorithm after each measurement. This information can then be used to reposition the ZLP if any drifting has occurred. The positioning of spectra on the photo-diode array is controlled by the voltage scan module (VSM), see fig(2.3). The VSM works by applying an accurate voltage, V, to the drift tube of the PEELS, fig(2.5), which accelerates the electrons moving through the magnetic field and consequently the position of the spectrum on the photo-diode array is shifted.

Using the same region of the photo-diode array manages the problem of gain variation but does not address the problem of memory effect. In a study of the properties of the PEELS [27] it was shown that the memory effect decays independently of the integration time used and that the decay constant is \( \approx 2.5 \) readouts. By employing the VSM to deflect the energy loss spectra away from the photo-diode array in between each measurement, 3 readouts can be performed while no illumination is incident on the array. This procedure is implemented to reduce the error caused by memory effect.
2.3 Data Collection

To obtain high quality diffraction data it is important that a number of experimental procedures are employed before and during data collection. These procedures deal mostly with the difficulty of obtaining an accurate scale in steps of $Q, \Delta Q$, as the diffraction pattern is stepped across the entrance aperture to the PEELS. However they also deal with the difficulties of collecting accurate data due to instrumental limitations, in particular the limited dynamic range of the photo-diode array.

2.3.1 Scale Linearity

Clearly it is important that the diffraction pattern is measured along its diameter, otherwise $Q$ will not increment over a uniform distance as the diffraction pattern is stepped across the aperture of the PEELS; this non-linearity in the scale will then introduce error into the measurement. To overcome this problem, before a diffraction pattern is collected the central maximum of the diffraction pattern is manually positioned directly above the entrance aperture to the PEELS. As the scanning of the diffraction pattern follows a straight line any line passing through the centre of the diffraction pattern must be a diameter of the diffraction pattern.

Calibration of the scale of $Q$ in a diffraction pattern is performed by comparison with a standard. The standard is obtained by measurement of the diffraction pattern of a polycrystalline thin film, usually platinum or aluminium. Peaks in the diffraction pattern of polycrystalline materials arise from electrons being scattered by different planar orientations within the unit cell of the material. The orientation of these planes is normally given in reciprocal space by the Miller indices $h, k, l$. Peaks in the diffraction pattern of polycrystalline materials therefore correspond to different combination of the indices $h, k, l$. For a $fcc$ unit cell the interplanar spacing $d_{hkl}$ is given by

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2},$$

(2.45)
where \( a \) is the cell constant. \( d_{hkl} \) is also related to \( Q \), the wave vector by

\[
d_{hkl} = \frac{2\pi}{Q}.
\]  

(2.46)

Using these relationships and knowing which interplanar spacings cause particular peaks in the diffraction pattern, the scale, \( \Delta Q \), can be calculated. It is important that the data used for calibration is collected under the same electron-optical configuration as the normal data to ensure that the scales are the same; difficulties are most easily minimised by performing the two measurements consecutively.

2.3.2 Dynamic Range

In many cases a diffraction pattern has an inherently large dynamic range (\( \approx 2 \times 10^4 \)) varying from the very intense central maximum to the dim intensities obtained at large scattering vectors \( \geq 3\text{\AA}^{-1} \). By comparison the photo-diode array has quite a limited dynamic range (\( < 10^3 \)). This means that the diffraction pattern cannot be collected using a single illuminating intensity. Modification of the illuminating intensity is achieved during data collection by changing the integration time to keep the illumination within the dynamic range of the photo-diode array whilst maintaining good counting statistics. The decision as to when to increase the integration time is achieved by monitoring the signal to noise ratio of the ZLP in each collected spectra. When the signal to noise ratio falls below a nominal value, the integration time is increased. In a typical collection the integration time may be changed up to five times. At large scattering angles this problem is compounded, because the readout noise of the silicon diodes is comparable to the electron signal. This noise may be reduced by cooling the array in the PEELS; a built in Peltier cooler performs this task, fig(2.5). However the reduction in readout noise is achieved at the expense of an increased number of readouts over which the memory effect decays, increasing the total data collection time.

Controlling the integration time increases the effective dynamic range achievable
and allows a larger portion of the diffraction pattern to be collected [28]. However even with the increased dynamic range, measurements of the diffraction pattern in the vicinity of \( Q = 0 \) cannot be made. The intensity in this region, which is called the central maximum of the diffraction pattern, readily saturates the photo-diode array and, to protect the photo-diode array from permanent damage, an automatic attenuation of the incident beam is enforced by the software. Though the intensity in the central maximum of the diffraction pattern can be reduced in a number of ways, it is so large, when compared to the diffraction peaks, that any configuration of the electron optics that allows it to be measured excludes measurement of any of the other features present in the diffraction pattern.

This difficulty is overcome by not taking measurements of the central maximum of the diffraction pattern. To do this, a large voltage is applied to the drift tube of the PEELS by the VSM, see fig(2.5), to deflect electrons away from the photo-diode array while the central maximum of the diffraction pattern is scanned across the entrance aperture of the PEELS during collection. The decision as to when to deflect the electrons away from the photo-diode array is made by determining whether a nominated number of counts in any channel of a recorded spectrum has been exceeded, this value is normally set at 14000 counts which is less than the saturation value of \( \approx 16000 \) counts. A second decision as to when normal data collection should resume is made by the operator, who will enter an estimate for the width of the central maximum before beginning data collection. Then after the initial decision has been made as to the onset of the central maximum during data collection, the VSM will be directed to keep the electrons deflected away from the photo-diode array until the width of the central maximum, supplied by the operator, has been exceeded.

### 2.4 Data Processing

The diffraction data that has been collected is not yet in a form that will allow processing to obtain \( G(r) \), fig(2.6). At this point approximately 1024 datapoints
have been collected; however the centre of the diffraction pattern has not been determined, the data itself incorporates a range of different integration times, seen as steps in fig(2.6), and the elastic portion of the diffraction pattern has not been measured. All the manipulations that need to be made to the recorded data to obtain \( G(r) \) are performed offline through another custom function added to the GATAN EL/p software.

**Figure 2.6:** This diagram shows diffraction data collected using the EFDP technique of Cockayne and McKenzie, before the data has been processed into a form from which \( G(r) \) can be derived.

To determine the elastic scattering component of the diffraction pattern the ZLP is integrated in each of the collected spectra. There is however a difficulty in performing this task at low and high \( Q \) values. At low \( Q \) values the ZLP may be convolved with the tail of a broad plasmon peak, fig(2.7), while at high \( Q \) values it may be difficult to distinguish the signal from the noise. Both of these problems have been solved by applying a second difference filter to the spectral data [9].

The problem of overlap between the ZLP and the plasmon peak is overcome because the Gaussian shape of the ZLP forms a sharp peak in the differentiated
spectrum, whilst the tail of the plasmon peak, due to its slowly varying curvature, does not contribute significantly to the differentiated spectrum, fig(2.7) [28]. The problem of separating the signal from the noise is overcome because the second difference filter is a form of low pass filter and constant background noise is removed from the second difference spectrum. After filtering, the positive portion of the of ZLP in the second difference spectrum is integrated and the elastic contribution of the diffraction pattern is measured. The intensity measured in this manner is directly proportional to the intensity that would be measured without filtering, as has been shown by Keast [29]. Following Keast the ZLP is assumed to have a Gaussian profile and as such, the ZLP can be defined by the function \( D(E) \) where

\[
D(E) = Ae^{-bE^2}. \tag{2.47}
\]

In eqn(2.47) \( A \) is the amplitude of the Gaussian function and \( b \) defines its width. After application of the second difference filter the profile of the ZLP is described by the second derivative of \( D(E) \) which is given by

\[
D''(E) = A \left[ 4b^2 E^2 e^{-bE^2} - 2be^{-bE^2} \right]. \tag{2.48}
\]

To determine the elastically scattered component of the diffraction pattern, the positive portion of \( D''(E) \) is integrated. This is effected by integrating \( D''(E) \) between the limits \( E = \pm \frac{1}{\sqrt{2b}} \) the values at which \( D''(E) \) intersects the horizontal axis. Performing this integration gives

\[
\int_{-\frac{1}{\sqrt{2b}}}^{\frac{1}{\sqrt{2b}}} D''(E) dE = A \left[ -2\sqrt{2be^{-\frac{1}{b}}} \right]. \tag{2.49}
\]

Integrating \( D(E) \) between the same limits gives

\[
\int_{-\frac{1}{\sqrt{2b}}}^{\frac{1}{\sqrt{2b}}} D(E) dE = A \left[ \sqrt{\frac{\pi}{b}} erf\left( \frac{1}{\sqrt{2}} \right) \right]. \tag{2.50}
\]

Through comparison of eqn(2.49) and eqn(2.50) it can be seen that the integrations of \( D(E) \), the ZLP, and \( D''(E) \), the second difference filtered ZLP, differ only by a multiplicative constant that is dependent upon \( b \). Thus use of second
difference filtering to collect the elastically scattered component of the diffraction data is valid whilst \( b \) remains constant.

**Figure 2.7:** The second difference of the energy loss spectrum (ELS) is determined to separate the overlapping regions of the ZLP and the plasmon peak.

Having obtained the elastically scattered component of the data, the next manipulation of the data that must be performed is to scale the data in fig(2.6) such that there are no differences in intensities due to the use of different integration times. The scaling is possible because during collection when a change in integration time was made, an overlapping region of 40 channels was collected at the new integration time. By plotting the overlapping intensities after the change in integration time against the overlapping intensities before the change in integration time a constant of proportionality, \( m \), can be measured, where \( m \) is theoretically equal to \( \frac{t_2}{t_1} \) the ratio of the different integration times. By multiplying all the data collected before the change in integration time by \( m \) the intensities within the spectrum are scaled. The overlapping data is then removed and the process is repeated for the next change in integration time [29]. This scaling procedure also benefits from the second difference filtering of the experimental data, as the constant background noise, which changes the value of the
constant of proportionality, has been removed.

As the central maximum of the diffraction pattern was not measured, fig(2.6), a method for determining the centre of the diffraction pattern must be found. This is because if the centre is not determined accurately a constant is added to the scale of $Q$ and error is introduced to the resulting $G(r)$. By measuring both sides of the diffraction pattern, symmetry can be used to determine the centre of the diffraction pattern. After determining the centre of the diffraction pattern the redundant data, due to the symmetry of the diffraction pattern, is removed and the spectrum is calibrated. In a standard collection $\Delta Q$ is $\approx 0.005 \text{Å}^{-1}$, see fig(2.8).

![Calibration Curve](image)

**Figure 2.8**: A calibration curve measured from polycrystalline aluminium. The curve is determined by plotting the channel number of the peaks in the diffraction pattern against the reciprocal of their corresponding interplanar spacings. The gradient of this curve gives the scale, $\Delta Q$, of the diffraction pattern.

The next step in calculating $G(r)$ involves converting the intensity $I(Q)$ into $\Phi(Q)$, the reduced intensity function. To perform this conversion the values of $f(Q)$ at specific $Q$ for a given atom type need to be known. These values are
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obtained from tables produced by Doyle and Turner [30] who applied the Born approximation, see Section 2.1.1, to derive them. As well, the value of $N$ in eqn(2.24) needs to be determined. This is done by differentiating the squared deviations between $N \phi^2(Q)$ and $I(Q)$ with respect to $N$ at large $Q$ values, $Q \geq 3.0\text{Å}$, [15]. By setting the result of the differentiation equal to zero, the value of $N$ which gives the smallest difference between $N \phi^2(Q)$ and $I(Q)$ can be determined, see fig(2.9).

$$d \left\{ \sum_{\text{large } Q} [I(Q) - N \phi^2(Q)]^2 \right\} \over dN = 0$$

$$\sum_{\text{large } Q} {I(Q) \phi^2(Q) \over \phi^2(Q) \phi^2(Q)} = N.$$  \hfill (2.51)

The reason for performing the calculation in eqn(2.51) at large $Q$ is because self scattering dominates the diffraction pattern at these $Q$ values and $I(Q) \approx N \phi^2(Q)$.

![Graph showing $I(Q)$ and $N \phi^2(Q)$ vs. $Q$](image)

**Figure 2.9:** Shows $N \phi^2(Q)$ and $I(Q)$, where the value of $N$ that is used has been determined using eqn(2.51).

After obtaining $\Phi(Q)$ (see fig(2.10)) from the experimental data it is now possible to calculate $G(r)$ using eqn(2.25). In eqn(2.25) it is noted that the integral is performed over all $Q$ from $0-\infty$; however the experimental data is truncated
at specific $Q$ values, $Q_{\text{max}}$ and $Q_{\text{min}}$, which are normally $4\text{Å}^{-1}$ and $0.05\text{Å}^{-1}$ respectively. Eqn (2.25) then becomes

$$G(r) = \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} \Phi(Q) \sin(Qr) dQ. \quad (2.52)$$

Truncating the experimental data is equivalent to multiplying $\Phi(Q)$ by a step function, $A(Q)$.

$$\Phi_{\text{expt}}(Q) = \Phi(Q) A(Q), \quad (2.53)$$

where $A(Q)$ is given by

$$A(Q) = \begin{cases} 
1 & Q_{\text{min}} \leq Q \leq Q_{\text{max}} \\
0 & Q < Q_{\text{min}} \text{ or } Q > Q_{\text{max}} 
\end{cases}$$

The subsequent Fourier sine transformation of $\Phi_{\text{expt}}(Q)$ will produce a $G(r)$ which is convolved with a sinc function.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Graph of $\Phi(Q)$. $\Phi(Q)$ does not converge to zero at $Q_{\text{max}}$.}
\end{figure}

This not only broadens the peaks in $G(r)$ but produces additional high frequency ripples or "ringing". These effects can combine to make $G(r)$ unusable.
Figure 2.11: $\Phi(Q)$ has been damped using the Lorch damping function.

To reduce the ringing, $\Phi_{exp}(Q)$ is damped at large $Q$, making $\Phi_{exp}(Q)$ converge smoothly to zero at $Q_{max}$, see fig(2.11).

Figure 2.12: Displays $G(r)$ curves determined using the damped and undamped $\Phi(Q)$ curves in fig(2.10) and fig(2.11) respectively. The $G(r)$ curve obtained from the undamped $\Phi(Q)$ curve exhibits high frequency ripples.
This can be represented mathematically by

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} \Phi_{expt}(Q) L(Q) \sin(Qr) dQ.$$  \hspace{1cm} (2.54)

where $L(Q) = \text{sinc}(\frac{Q}{Q_{max}})$ is the Lorch damping function [31]. Using damping reduces the effect of ringing, see fig(2.12), but it also decreases the resolution that is obtainable. However even with the loss in resolution nearest neighbour distances can still be determined to an accuracy of 0.02Å [8].

Fig(2.13) shows a $G(r)$ measured from polycrystalline platinum using the EFDP technique. The first four nearest neighbours all agree with the accepted values for the fcc structure of platinum [32] to within ± 0.02Å. The total collection time was about half an hour and the data was processed off line, taking about five minutes.

![Graph of G(r) for polycrystalline platinum showing the first 4 nearest neighbour distances; the distances agree with accepted values to within ± 0.02Å. The accepted values are highlighted by a *.

Figure 2.13: $G(r)$ curve for polycrystalline platinum showing the first 4 nearest neighbour distances; the distances agree with accepted values to within ± 0.02Å. The accepted values are highlighted by a *.
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2.4.1 Conclusion-Energy Filtered Electron Diffraction

Through the coupling of a TEM and a PEELS, Cockayne and McKenzie have developed a technique that is capable of energy filtering diffraction patterns. In this Chapter energy filtering was used to select the elastically scattered component of the diffraction pattern, $E = 0$; however it could also be used to select the inelastic portion of the diffraction pattern $E > 0$. Essentially through the use of EFDP the intensity in a diffraction pattern can be measured over a range of scattering vectors, $Q$, and energy losses, $E$, i.e $I(Q, E)$, which provides access to a wealth of information about the material.
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CHAPTER 3

Plasmon Dispersion Analysis

3.1 Introduction

In developing a technique that could measure the elastically scattered component of an electron diffraction pattern, Cockayne and McKenzie [1, 2] had simultaneously developed a technique that could measure the inelastically scattered component of an electron diffraction pattern, the only difference between the two techniques being the portion of the electron energy loss spectrum that was employed in an analysis. In fig(3.1) a standard electron energy loss spectrum is displayed. To determine the elastically scattered component of a diffraction pattern, region A, defined by two vertical dashed lines, is analysed in each of the electron energy loss spectra measured at different positions, Q, in the diffraction pattern. In a similar fashion the inelastically scattered component of the diffraction pattern can be determined by analysing region B from each of the measured
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**Figure 3.1:** The two regions, A and B, marked on the electron energy loss spectrum are used to measure the elastic and inelastic components of an electron diffraction pattern.

electron energy loss spectra. Region $B$ is also marked on fig(3.1) and extends to large energies (represented by an arrow). Note that the energy value in the spectrum at which the elastically scattered component finishes and the inelastically scattered component begins is arbitrarily defined. This energy value is chosen so that intensity measured in region $A$ is mostly due to elastic scattering processes and intensity measured in region $B$ is mostly due to inelastic scattering processes. This value will depend upon the material being studied.

The acquisition of the inelastic portion of the electron diffraction pattern is quite simply effected by changing the region of the electron energy loss spectrum that is recorded. However, the analysis of the characteristic features in this region is quite complicated when compared with that of the elastically scattered region. This is because, whilst the elastically scattered electron’s angular distribution is effected only by the change in momentum that has occurred during scattering, the inelastically scattered electron’s angular distribution is effected by both the change in momentum and the energy lost by the electron during scattering. Furthermore there are a number of different electronic excitations through which
the scattered electron may lose energy. Essentially, in measuring the inelastic region of an electron energy loss spectrum, the electronic structure of a material is being examined, and thus a reasonable working knowledge of atomic and solid state physics is required to interpret the features present in this region.

A starting point for understanding the electronic structure of a material is the energy level diagram of a solid, see fig(3.2).

![Energy level diagram of a solid](image)

**Figure 3.2:** Energy level diagram of a solid.

In this diagram the atoms within the solid are represented by periodic potentials, shown as dashed curves. The inner shell or bound electrons are found localised within the atomic potential and are separated into discrete energy levels. Outer shell electrons also called valence electrons have a continuum of possible energy levels that they may occupy below the Fermi energy \( (E_F) \); these levels are shown by a shaded region beneath \( E_F \), where \( E_F \) is the energy of the level which has a 0.5 probability of being occupied by an electron [3]. Above the Fermi energy is a continuum of unoccupied energy levels, also shaded, into which bound or valence electrons may be excited.

From the energy level diagram it is clear that an electron passing through a material can lose energy by exciting either a bound or a valence electron into
an unoccupied energy level above the Fermi energy of the solid. However the diagram does not make it clear that an electron can also lose energy by causing collective oscillations of the valence electrons called plasma resonances [4]. This is possible because the valence electrons interact with one another through long range Coulombic forces. The plasma resonance can also be thought of as a pseudoparticle, using quantum theory, with an energy given by $E = \hbar \omega$, where $\hbar$ is Planck's constant and $\omega$ is the frequency of the plasma resonance. This pseudoparticle is commonly called a plasmon.

In this Chapter it is the plasmon excitation that will be closely examined because of its dependence on momentum transfer. This momentum dependence, described by the plasmon dispersion relation, is well suited for analysis using the technique of Cockayne and McKenzie [1] which resolves electron energy loss spectra according to momentum transfer. Also as the plasmon dispersion relation contains information about the electronic structure of a material, plasmon dispersion analysis (PDA) has the potential to reveal new information about a material.

PDA is not a new technique. Much of the fundamental theory describing plasmon dispersion was developed during the 1950's by Pines, Bohm and Nozières [5, 6, 7, 8] and since then a vast amount of plasmon dispersion data has been collected [9, 10, 11]. However most of this data is derived from alkali metals, due to the fact that their electronic and atomic structure are more accurately approximated by assumptions made in the theory of plasmon dispersion than are the electronic and atomic structure of other types of materials. In this Chapter PDA will be used to investigate amorphous materials.

In order to quantify the usefulness of a detailed study using PDA as a means to characterise amorphous materials, a range of amorphous carbon solids with different electronic and atomic structures has been investigated. As well, attempts have been made to automate PDA as it is foreseen that the ability to use PDA
in conjunction with EFDP would enable sophisticated materials analysis. The results of this work and their implications, in terms of using PDA to characterise materials, forms the bulk of the material in this Chapter.

3.2 Inelastic Scattering

The inelastic scattering of a high energy electron by a thin film of material can cause a loss of energy by the electron and a change in its momentum. By measuring the energy of the scattered electron, using an electron energy loss spectrometer, an electron energy loss spectrum can be formed. This spectrum is characteristic of the electronic and atomic structure of the material under investigation. Typically the high energy electron is inelastically scattered by the valence or bound electrons of an atom within the material. This produces distinctive energy losses within the range of 0-100eV for valence electron scattering and >40eV for bound electron scattering [12]. Clearly there is some overlap in the amount of energy lost by the different scattering processes.

![Graph showing ionisation loss edges for carbon and nitrogen](image)

**Figure 3.3:** Ionisation loss edges for carbon and nitrogen. The electron energy loss spectrum was obtained from carbon-nitride.

The situation in which energy is transferred from a high energy electron to a
bound electron will only occur if there is enough energy available to ionise the atom, that is if $E \geq E_F - E_B$ [12], where $E_B$ is the binding energy of the bound electron. When such an energy transfer does take place a peak is formed in the electron energy loss spectrum. This peak is called an “ionisation loss edge”. In fig(3.3) two ionisation loss edges are shown, the carbon $K$ shell loss edge at 284eV ($K$ shell being the name of the inner shell that the bound electron was excited from) and the nitrogen $K$ shell loss edge at 401eV.

Although bound electron scattering forms a significant contribution to any electron energy loss spectrum, the majority of inelastic collisions at low $Q$ are caused by the scattering of high energy electrons from valence electrons. During the scattering event the energy exchanged can cause a number of different electronic excitations within the material. If the energy is transferred to a single valence electron it may cause an inter or intraband transition. It is also possible that the energy transferred may excite a plasmon fig(3.4). Plasmons may be excited in the bulk of the material or on its surface; it is the bulk excitation with which PDA is concerned and whose theoretical description is presented in the following Sections.

![Diagram of bulk plasmon excitation](image_url)

**Figure 3.4:** A conceptual diagram of a bulk plasmon excitation caused by an inelastic scattering event.
3.2.1 Dielectric Theory

The plasmon scattering event is usually described using either quantum mechanics [13] or dielectric theory [14], a subbranch of electromagnetism. When using quantum mechanics a Hamiltonian equation representing the interaction between a high energy electron and a single valence electron is formulated and then solved. The solution is then generalised to the situation of a collective interaction between a group of electrons. Alternatively the dielectric approach seeks to determine the dielectric response function $\varepsilon(\omega, Q)$ of a material in the presence of a moving charged particle. Of these two descriptions the dielectric description is normally used because it intrinsically accounts for a group particle response by a material to an external disturbance, in this case the high energy electron. Conversely the quantum mechanical approach becomes more complicated as it is extended to account for a many body response. For these reasons the dielectric formalism is now used to briefly describe plasmon scattering and dispersion.

3.2.2 Dielectric Response Function

In dielectric theory the reaction of an ensemble of valence electrons to the presence of a moving charged particle may be characterised by $\varepsilon(\omega, Q)$, which is a function of both the wavelength and frequency of the electromagnetic disturbance produced in the material by the particle. The particle itself is represented by a point charge, $f(r, t)$ moving with a velocity $v$ [15].

$$f(r, t) = -e \delta(r - vt). \quad (3.1)$$

The field produced in the solid by the moving charge is given by Poisson’s equation [16] and is thus both space and time dependent.

$$\varepsilon(\omega, Q) \nabla^2 V(r, t) = -4\pi f(r, t), \quad (3.2)$$

where $V(r, t)$ is the electrostatic potential. From electromagnetic theory the power dissipation density [17] in a medium due to dielectric losses, $P(\omega, Q)$, is
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given by

\[ P(\omega, Q) = \frac{1}{4\pi} I(\omega) \frac{\partial D(\omega, Q)}{\partial t}, \]  

(3.3)

where \( I(\omega) \) is a transverse electromagnetic wave of the form \( I(\omega) = I e^{-i\omega t} \). \( D(\omega, Q) \) is the displacement vector of electromagnetic theory and is a function of the free charge in the medium, the free charge being in this instance the moving charged particle. The power is dissipated by the electric field which accompanies the charge \([18]\), which causes irreversible Joule heating in the material. From the standard relationship \([17]\)

\[ D(\omega, Q) = \varepsilon(\omega, Q) \nabla V(\omega, Q), \]  

(3.4)

where \( V(\omega, Q) \) is the Fourier transform of \( V(\mathbf{r}, t) \), it is possible to determine the form of \( P(\omega, Q) \),

\[ P(\omega, Q) = \frac{\omega}{8\pi} \text{Im} \left( \frac{1}{\varepsilon(\omega, Q)} \right) D^2(\omega, Q). \]  

(3.5)

In eqn(3.5) \( \text{Im} \left( \frac{1}{\varepsilon(\omega, Q)} \right) \) is the imaginary part of the reciprocal of the dielectric response function and is known as the energy loss function. \( P(\omega, Q) \) thus describes the energy lost by the charge as it moves through the material \([17]\). Hence through determination of \( \varepsilon(\omega, Q) \) it should be possible to estimate the amount of energy lost in a plasmon excitation and to establish a relationship for the dispersion of the plasmon energy with \( Q \), where \( Q = |Q| \).

3.2.3 The Jellium Model

The determination of \( \varepsilon(\omega, Q) \) is possible in only a few simple situations \([19]\), and so a number of models have been developed that give approximate relationships for \( \varepsilon(\omega, Q) \). One such model is the Jellium model.

The Jellium model, which is closely related to the Drude model for conduction in metals \([20]\), is a simple semiclassical description of a solid in which the valence electrons are assumed to be independent particles, moving in a constant background potential formed by the lattice of ion cores. The valence electrons interact
with each other through Coulombic forces and this interaction can be thought of as causing the electrons to behave as a set of coupled oscillators.

Using this model $\varepsilon(\omega, \mathbf{Q})$ can be determined for small scattering angles [17], that is $\mathbf{Q} \simeq 0$. This gives the long wavelength dielectric response $\varepsilon(\omega, 0)$ or $\varepsilon(\omega)$ which can be compared with optical data. $\varepsilon(\omega)$ is obtained from the equation of motion of a free electron in an electric field, where the effect of the ion core lattice is included by defining an effective mass, $m$, for the electron that differs from its rest mass, $m_e$. A damping constant, $\gamma$, can be included in the equation of motion to account for collisions between electrons. $\gamma$ is the reciprocal of the relaxation time which is defined as the average time between electron collisions. The equation of motion is then

$$m \frac{d^2 \mathbf{r}}{dt^2} + m\gamma \frac{d \mathbf{r}}{dt} = -eI(\omega). \quad (3.6)$$

Eqn(3.6) describes the force on the electron due to a time dependent harmonically oscillating electric field. The solution to this equation is

$$\mathbf{r} = \frac{e}{m} I(\omega) \frac{1}{(\omega^2 + i\gamma \omega)}. \quad (3.7)$$

The dipole moment for an electron is defined as $-e \mathbf{r}$. The polarisation of a material is the dipole moment per unit volume, expressed as

$$P = -n e \mathbf{r}, \quad (3.8)$$

where $n$ is the number of electrons per unit volume.

In linear media the electric displacement is defined as $D(\omega) = I(\omega)\varepsilon(\omega)$ and also as $D(\omega) = I(\omega) + 4\pi P(\omega)$. Combining these two relationships for $D(\omega)$ with eqns(3.7, 3.8) a simple expression for the dielectric function is obtained

$$\varepsilon(\omega) = 1 - \frac{w_p^2}{w(w + i\gamma)}, \quad (3.9)$$

where the plasmon frequency is given by

$$w_p = \left( \frac{n e^2}{\varepsilon_0 m} \right)^{\frac{1}{2}}.$$
3.2.4 Lindhard’s Model

The dielectric function developed from the Jellium model in Section 3.2.3 was derived for small \( Q \). A more sophisticated model is needed if a mathematical relationship describing plasmon dispersion is to be established. Such a model was provided by Lindhard [21] who extended the Jellium model to higher \( Q \) values by assuming that correlation effects and spin exchange caused by Coulombic interaction between the electrons when they are oscillating is negligible [19]. This assumption is known as the random phase approximation [22].

Lindhard’s dielectric response function is

\[
\varepsilon_L(\omega, Q) = 1 - \frac{4\pi \epsilon^2}{Q^2} D(\omega, Q),
\]

(3.10)

where

\[
D(\omega, Q) = \int \frac{dk}{4\pi^3} \frac{f_\omega(k + Q) - f_\omega(k)}{E(k + Q) - E(k) + \omega + i\gamma}.
\]

(3.11)

In eqn(3.10) \( f_\omega(k) \) is the equilibrium Fermi function for a free electron of wave vector \( k \) [20], and \( E(k) \) is the energy of a free electron of wave vector \( k \).

3.2.5 Plasmon Dispersion Relationship

The condition that \( \varepsilon(\omega, Q) = 0 \) determines the frequencies of the longitudinal modes of oscillation of the electron gas [23] or plasmon modes. This condition can be understood by recognising that the longitudinal wave will produce a depolarising field \( I(\omega) = -4\pi P(\omega) \) and so \( D(\omega) = 0 \) as \( D(\omega) = I(\omega) + 4\pi P(\omega) = 0 \). As it is also true that \( D(\omega) = \varepsilon(\omega)I(\omega) \), the relationship is satisfied by \( \varepsilon(\omega) = 0 \).

Application of this condition to Lindhard’s dielectric function, in the limit that \( \frac{1}{\gamma} \) approaches zero (the approximation for a free electron gas), allows the plasmon dispersion relationship to be established. First \( \varepsilon_L(\omega, Q) \) is expanded in powers of \( Q \) [23, 24]. This gives

\[
\varepsilon_L(\omega, Q) = 1 - \frac{\omega^2}{\omega^2} - \frac{6 \omega^2 E_F}{5 \omega^4} \frac{1}{m} Q^2 - \frac{\omega^2}{\omega^4} \left( \frac{12}{7} \frac{E_F^2}{\hbar^2 \omega^2} + \frac{1}{4} \right) \frac{\hbar^2 Q^4}{m^2} + ....
\]

(3.12)
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Then by setting the expanded form of $\varepsilon_L(\omega, Q)$ to zero and ignoring all powers of $Q$ greater than $Q^2$ the plasmon dispersion relationship for a free electron gas is established.

$$E_p(Q) = E_p(0) + \alpha \frac{\hbar^2}{m_e} Q^2,$$

(3.13)

where $\alpha = \left(\frac{3}{8}\right) \frac{E_F}{E_p(0)}$, $E_F$ is the Fermi energy and $E_p(0)$ is the plasmon energy when $Q = 0$. It is this relationship that is monitored using PDA and used to fingerprint the different carbon solids.

3.2.6 Cut-Off Wave Vector

As the wave vector increases, the damping of the plasmon oscillation becomes more pronounced until a cut-off wave vector, $Q_c$, is reached [9] where it becomes possible for the plasmon to transfer all its energy to a single electron which is then excited into an unoccupied energy level [25]. The interaction between the plasmon and the electron must satisfy the rules of conservation of energy and momentum, which require that

$$E = \left(\frac{\hbar^2}{2m_e}\right)(Q + Q_i)^2 - \left(\frac{\hbar^2}{2m_e}\right)Q_i^2 = \left(\frac{\hbar^2}{2m_e}\right)(Q^2 + 2Q \cdot Q_i),$$

(3.14)

where $E$ is the energy and $\hbar Q$ is the momentum transferred to an electron with an initial momentum $\hbar Q_i$ and rest mass $m_e$.

The smallest value of $Q_i$, needed to satisfy this relationship occurs when $Q_i$ is parallel to $Q$ and $Q_i$ is itself as large as possible. The largest average value for $Q_i$ is obtained if $Q_i$ lies on or near the Fermi level; in this case $Q_i = Q_F$ where $Q_F$ is the Fermi wave vector. In eqn(3.14) if $E_p(Q)$ is substituted for $E$ and $Q_F$ is substituted for $Q$, where $Q$ and $Q_F$ are parallel, the relationship can be rewritten as

$$E_p(0) + \alpha \frac{\hbar^2}{m_e} Q_c^2 = \left(\frac{\hbar^2}{2m_e}\right)(Q_c^2 + 2Q_c Q_F).$$

(3.15)

Following Egerton [19], if it is assumed that $\alpha$ has a value of approximately 0.5,
an approximate value for $Q_c$ can be determined,

$$Q_c = \frac{E_p}{\hbar v_F}.$$  \hfill (3.16)

### 3.2.7 Multiple Plasmon Scattering

Single scattering of a plasmon is only one of a number of possible inelastic scattering processes that contribute to the electron energy loss spectrum. In traversing a specimen there is a finite possibility that an electron may have more than one collision, each of which can be either elastic or inelastic. In the situation where more than one collision does occur the electron is described as being multiply scattered. In the low loss region of the electron energy loss spectrum (0-100eV) the dominant peaks observed are due to single and multiple scattering events involving one or more plasmon excitations. These combination scattering effects overlap each other and complicate the observed energy loss spectrum, and, for example, make it difficult to measure the plasmon dispersion relationship due to single plasmon scattering events.

Typically a process occurs in which there is scattering from several plasmons $\hbar Q_1, \hbar Q_2, \ldots, \hbar Q_n$ in combination with a single elastic scattering event $\hbar Q_c$. The total momentum transfer is then given by $\hbar Q = \hbar Q_c + \hbar Q_1 + \hbar Q_2 + \ldots + \hbar Q_n$. These combination scattering events become more probable when there are high energy elastically scattered electrons propagating through the specimen.

To account for these multiple scattering events involving plasmon excitations a scattering cross section is developed which includes only the dominant scattering processes [26]. This scattering cross section, which depends upon the momentum and energy loss of the electron, can be written as

$$S(\omega, Q) = \frac{K_1 \sigma(Q) \omega_p^2(Q)}{(\omega^2 - \omega_p^2(Q))^2 + (\omega \Gamma(Q))^2} + \frac{K_2 F^2(Q) \sigma(0) \omega_p^2(0)}{(\omega^2 - \omega_p^2(0))^2 + (\omega \Gamma(0))^2}$$

$$+ K_3 \int_0^\infty \frac{\sigma(Q_1) \omega \Gamma(Q_1) \omega_p^2(Q_1)}{(\omega^2 - \omega_p^2(Q_1))^2 + (\omega \Gamma(Q_1))^2} \times \frac{\sigma(Q_2) \omega \Gamma(Q_2) \omega_p^2(Q_2)}{(\omega^2 - \omega_p^2(Q_2))^2 + (\omega \Gamma(Q_2))^2} dQ_1.$$  \hfill (3.17)
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For this equation to be exactly comparable to the experimentally derived data the zero loss point spread function should be convolved with eqn(3.17) to take into account the effects of instrumental broadening.

In eqn(3.17) $K_1$, $K_2$, and $K_3$ are empirically determined constants, $\omega_p(Q)$ is given by the plasmon dispersion relationship, and $\Gamma(Q)$, which is proportional to $\frac{1}{\tau}$, where $\tau$ represents the plasmon lifetime, is the factor determining the width of the plasmon peak. $F(Q)$ is the amplitude of elastic scattering and $\sigma(Q)$ is the cross section for plasmon scattering given by

$$\sigma(Q) = C \frac{1}{Q^2 + Q_0^2} \quad (3.18)$$

where $C$ and $Q_0$ are constants.

The three terms in eqn(3.17) arise from different scattering events, they are respectively:

- a single plasmon scattering event of momentum transfer $Q$.

- an elastic scattering event causing a momentum transfer $Q$ in combination with a plasmon scattering event of zero momentum transfer. This particular scattering process has the effect of redistributing zero momentum transfer plasmon scattering events throughout the diffraction pattern.

- a plasmon scattering event with momentum transfer $Q_1$ followed by a plasmon scattering event with momentum transfer $Q_2$, in which the total momentum transferred is $Q = Q_1 + Q_2$.

Other multiple scattering events, including an elastic scattering event combined with scattering from a plasmon of non-zero momentum transfer are neglected because their contribution to the observed intensity in the electron energy loss spectrum is small. Contributions from triple plasmon scattering and plasmon scattering of non zero $Q$ combined with an elastic scattering event are also neglected.
3.2.8 Generalisation of the Lindhard Equation

Many different solids exhibit the phenomenon of plasmon dispersion. However the dispersive behaviour does not always display a quadratic dependence on the wave vector $Q$, as predicted by the Jellium model in eqn(3.13) [27]. This is because the quadratic $Q$ dependence arises from a model in which the valence electrons are approximated as free particles. Obviously solids for which this is not a reasonable approximation would not be expected to exhibit a quadratic dispersion.

The plasmon dispersion relationships of the carbon solids examined in this thesis do not display a strict quadratic dependence on $Q$. In this situation the Lindhard eqn(3.13) is generalised in an empirical fashion so that it can be used to compare the different carbon solids. The equation is generalised by replacing the quadratic power with $r$, an empirically determined constant.

$$\hbar\omega_p(Q) = \hbar\omega_p(0) + \alpha Q^r \left( \frac{\hbar^2}{m_e} \right).$$  \hspace{1cm} (3.19)

Using the generalised Lindhard eqn(3.19), eqn(3.15), describing the cut-off wave-vector, can also be modified to

$$\hbar\omega_p(0) + \alpha \left( \frac{\hbar^2}{m_e} \right) Q^r = \left( \frac{\hbar^2}{2m_e} \right) (Q_c^2 + 2Q_cQ_f).$$  \hspace{1cm} (3.20)

Experimentally the cut-off wave vector, $Q_c$, is determined by fitting the modified dispersion relation eqn(3.19) to the dispersion data for small $Q$ values and then looking for deviations from the relationship at large $Q$ values.

3.3 Experiment

The collection of electron energy loss spectra over a range of specific scattering vectors forms a three dimensional set of data with axes of intensity (or counts recorded by the photo-diode array within a specific integration time), wave vector and energy loss. A topological graph of a cube of such data is shown in fig(3.5), plotted with orthogonal coordinates.
Figure 3.5: A set of data collected from glassy carbon. The axes bounding the data set are intensity, wave vector and energy loss. Clearly distinguishable from a topological presentation of the data set is the elastic scattering peak, as well as the single, double and multiple scattering plasmon peaks.

The data set presented in fig(3.5) is measured from glassy carbon, and a number of features which are typical in low loss electron energy loss spectra are present. These include the elastic scattering peak, (the integration of the area under this peak gives the elastically scattered contribution to the diffraction pattern), the single plasmon peak and the double and multiply scattered plasmon peaks (which diminish in size and disperse with increasing $Q$).

The collection of the data in fig(3.5) is made using the same hardware as is used for the EFDP measurements outlined in Chapter 2, but with some minor modifications;

- The extent of the energy loss spectrum recorded is increased. This is because in EFDP analysis only the elastically scattered electrons are of interest and a relatively small energy loss window is employed. In plasmon dispersion analysis, however, the range of plasmon excitations extends between
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0-100eV and so an energy loss window of this order is employed.

- A modification to the software is required due to the difference between the probability for elastic scattering and the probability for inelastic scattering, by plasmon excitation, with increasing $Q$. In Chapter 2 the signal to noise ratio present in any collected spectra was measured by comparison of the intensity in the elastically scattered peak with the intensity of the background. When this ratio fell below a specified value the integration time for data collection was increased to maintain the quality of the counting statistics throughout the duration of the measurement. This procedure is not adequate though, for making plasmon dispersion measurements, because the intensity in the plasmon peak diminishes much more rapidly than in the elastically scattered peaks, see fig.(3.5). For this reason the signal to noise ratio in a plasmon peak might be quite poor even though the signal to noise ratio for the elastically scattered peak is still quite adequate. Essentially it is no use monitoring the elastically scattered peak to determine the signal to noise ratio for the plasmon peak. An initial idea to track one of the plasmon peaks during experimentation rather than the elastically scattered peak, to determine the signal to noise ratio, was rejected because of the complexity of the inelastic portion of the spectrum. This complexity combined with the drifting of the spectrum on the photo-diode array would make any peak searching algorithm relatively unstable.

Assume, for the moment, that the previous problem of determining the signal to noise ratio of the plasmon peak, whilst the experiment is in progress, has been solved. It would then be possible to increase the integration time when the signal to noise ratio became poor. At this point another difficulty is encountered, which is also due to the rapid decrease in the probability for plasmon excitation, because in general a simple change in the integration time is not sufficient to enable an adequate signal to noise ratio to be regained. Instead, to regain an adequate signal to noise ratio, an adjustment must be made to the optics of the TEM. The
adjustment could be a change in the size of the selected area aperture that is employed or the magnitude of the emission current that is used.

The simplest way to overcome both of these difficulties is by visual inspection of the data as it is being recorded, enabling a decision to be made as to whether or not the experiment should be interrupted so that the signal to noise ratio of the plasmon peak can be increased. To facilitate this decision-making process the EFDP software was modified so that each energy loss spectra was displayed immediately after it was recorded.

As well as modifications to the software there are a number of minor differences in the experimental technique employed to collect PDA data, which involve the measurement of low angle inelastically scattered data and the determination of the $Q$ scale. In Chapter 2 the difficulty in measuring small angle scattering data experimentally, due to the very intense central beam and the limited dynamic range of the detector, was mentioned in Section 2.3.2. In measuring EFDP data sets the problem was avoided by skipping over the central region of the diffraction pattern. However in performing PDA, electron energy loss measurements for low values of $Q$ are required, and measurements must be made as close as possible to the central beam without saturating the silicon photo-diode array. Though it is still not possible to measure the very centre of the diffraction pattern using the EFDP technique, very small scattering angles can be measured, through appropriate configuration of the electron optics, if data collection is started at $Q \approx 0$.

Beginning data collection at this point however leads to difficulties in determining the $Q$ scale of the data set. This is because only one side of the diffraction pattern is collected and symmetry cannot be used to determine the location of the centre of the diffraction pattern (as it is in EFDP see Section 2.4). To determine the scale of the data, the data collected must include an elastically scattered diffraction peak of known $Q$ value, which when combined with the $\Delta Q$ determined from a
standard measurement of a polycrystalline material can be used to determine the absolute scale of $Q$ in the PDA data set.

It was mentioned previously that there is a large variation in the intensity of the plasmon peak over a relatively small $Q$ range. This causes a practical limit of one illumination-integration configuration per data collection. For good quality data this limit forces the experimentalist to employ a piecemeal data collection procedure over the range of scattering vectors. Typically there might be three changes of integration setting over a range of $0.0 - 3.0\text{Å}^{-1}$. To ensure that the $Q$ scale is correct the different segments must contain overlapping features which can then be spliced together to produce a complete data set. This hands on approach to data collection makes PDA analysis a semi-automated technique as opposed to EFDP, which is a fully automated data collection and processing technique.

A final modification that must be made to the data before it can be used for processing is to ensure that the energy loss scales of each of the angularly resolved electron energy loss spectra are consistent. Even though a peak search algorithm is used to find and reposition the ZLP on the photo-diode array, this correction is not exact and there can be some variation in the position of the ZLP and consequently the scale of the energy loss spectra. This is corrected by manual recalibration of the spectrum ensuring that the ZLP appears at 0eV for each measurement, using the standard GATAN EL/p calibration function.

### 3.4 Data Processing

Data processing involves extracting the single plasmon peak position from the inelastic portion of the scattered data for each spectrum measured at a specific $Q$ value. The single plasmon peak position is determined using a non-linear least squares fitting technique to fit the plasmon peaks in the region from 0-100eV. Fortunately in the materials that were studied there were no additional peaks in this region due to other types of electronic excitations. Their presence would not
have greatly increased the difficulty of the problem as they do not disperse and are thus more easily modelled than the shifting plasmon peaks.

![Graph showing energy loss spectrum with peaks labeled as Peak 1 (q=0 Plasmon), Peak 2 (Single Plasmon), and Peak 3 (Double Plasmon).](image)

**Figure 3.6**: The low loss region of the electron energy loss spectrum is modelled by three separate peaks, determined from the inelastic scattering factor in Section 3.2.7. By modelling each of the separate peaks the single plasmon scattering contribution in this region can be determined and the dispersion of the single plasmon can be measured.

From fig(3.6) it can be seen that the task of peak fitting is complicated by the fact that a number of plasmon peaks may overlap, e.g. the single plasmon may overlap with the double plasmon and the double plasmon may also overlap with the multiple plasmon. The problem is further enhanced because the different plasmon peaks disperse with $Q$ at different rates. This means that if a particular feature (e.g. the presence of three peaks) is chosen to model the total plasmon contribution at low $Q$, this feature might not be present at a higher $Q$ making it difficult to use automated peak fitting procedures. At present this difficulty is overcome by performing the peak fitting manually. However this is tedious and further work needs to be done to automate this particular part of the data processing. The work would involve obtaining a thorough understanding of the possible excitations in this region and development of sophisticated modelling.
techniques to perform the extraction.

Using Genplot data analysis and plotting software, a function of the form

\[ f(Q) = c_o + \sum_{j=1}^{n} [c_j X_j(Q)], \quad (3.21) \]

was fitted to the inelastic scattering distribution in the region from 10-80eV, where the shape of \( X_j(Q) \) was determined from the inelastic scattering cross section of section 3.2.7. That is

\[ X_j(Q) = \frac{K_j \sigma_j(Q) \omega_{p_j}^2(Q)}{(\omega^2 - \omega_{p_j}^2(Q))^2 + (\omega \Gamma_j(Q))^2}, \quad (3.22) \]

where \( \Gamma_j(Q), \omega_{p_j}(Q) \), the cross sections \( \sigma_j(Q) \) and the constants \( K_j \) are treated as variable parameters and are determined by least squares fitting to the data. Using this technique a number of peaks were fitted to the data corresponding to each of the dominant plasmon scattering peaks in the low loss region of the electron energy loss spectrum, see fig(3.6).

How well \( f(Q) \) fits the data is determined by the \( \chi^2 \) goodness of fit statistic which is defined as

\[ \chi^2 = \sum_i \frac{1}{\beta_i^2} [f_i - f(Q_i)]^2, \quad (3.23) \]

where \( \beta_i \) is determined from the uncertainties in the measured data points. The optimum values of the parameters are then obtained by finding a minimum in the \( \chi^2 \) function with respect to each of the fitted parameters simultaneously.

\[ \frac{\partial}{\partial c_j} \chi^2 = \frac{\partial}{\partial c_j} \sum_i \left\{ \frac{1}{\beta_i^2} [f_i - f(Q_i)]^2 \right\} = 0. \quad (3.24) \]

Using the method of least squares then requires that an \( n \) dimensional space (\( n \) being the number of fitting parameters) is searched to find a global minimum, which gives the smallest value for the \( \chi^2 \) goodness of fit. Genplot employs the gradient search and function linearization methods to determine these parameters [28].
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By application of this technique the peak position of the single plasmon can be determined. The largest error measured in the peak position was $\pm 0.2\text{eV}$. This error value has been used in all subsequent calculations, even though in some situations the error was significantly less than this. Using this value effectively doubles the $\chi^2$ parameter, which has the effect of increasing the confidence level that the model represents the data from 95$-$99%. However the error in the fitting of the peak position is not the limiting factor in determining the peak position. The most important factor is the interpretation of how many peaks are actually present within the low loss region.

For the materials studied there were typically two to three peaks present which contributed significantly to the low loss region. In situations when $Q_c$ has been reached, the single or double plasmon may decrease markedly and it becomes difficult to tell exactly how many peaks are present within the plasmon envelope. Fortunately this problem is normally quite easy to avoid, as forcing the fitting algorithm to find three peaks when there are only two or vice versa will cause the algorithm to fail badly.

3.5 Materials Studied

In the study performed, a number of carbon solids were analysed along with aluminium, an alkali metal, which was used as a standard because of its close approximation by the free electron model, and because it has a well known plasmon dispersion relation [9, 10, 29].

The carbon solids studied were $C_{60}$, glassy carbon (a turbostratic form of graphite that contains only graphite-like bonding ($sp^2$ hybridized orbitals)), and three distinct forms of amorphous carbon differing in density and in the fraction of diamond like bonding ($sp^3$ hybridized orbitals). $C_{60}$ was chosen for the study as an example of a molecular system with the possibility of resonant plasmon modes in the spherical molecules. The study of the fullerenes has already received some
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<table>
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<th>$E_p$ (eV)</th>
<th>Density (gcm$^{-3}$)</th>
<th>$sp^2$ fraction</th>
<th>Reference</th>
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<td>1.55</td>
<td>1</td>
<td>[35]</td>
</tr>
<tr>
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<td>1.72</td>
<td>1</td>
<td>[36]</td>
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<td>0.9</td>
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<tr>
<td>Ion implanted ta-C</td>
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<td>2.4</td>
<td>0.5</td>
<td>[34]</td>
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<tr>
<td>ta-C</td>
<td>29.8</td>
<td>2.9</td>
<td>0.2</td>
<td>[32]</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of the carbon solids being investigated.

attention because of their unique closed caged structure consisting of a shell of high electron density enclosing a void of low electron density [30]. Since the dielectric response of a conduction sphere shows a resonant scattering, it might be expected that the spherical fullerene molecule might show resonances equivalent to those observed in the scattering of light by a conducting sphere [31].

The other disordered carbon solids examined in this study are tetrahedral amorphous carbon (ta-C) and evaporated (a-C). Ta-C is a dense form of carbon with a predominance of atoms in $sp^3$ bonding configurations [32]. In contrast evaporated amorphous carbon has a low density and is largely $sp^2$ bonded. A recent study of plasmon dispersion has been made in ion assisted evaporated films at low $sp^3$ content [33]. As well as the $sp^3$ content carbons studied here an ion implanted ta-C sample of intermediate $sp^3$ fraction [32]. These properties are summarised in table(3.1).

3.5.1 Materials Preparation

Electron transparent glassy carbon specimens were prepared from glassy carbon plates obtained from Chemicals Corporation (New York). The samples were prepared using ultramicrotomy. Films of $C_{60}$ were obtained by thermal evaporation of a powder (99.5% pure) onto a salt substrate, the substrate was subsequently dissolved and the films were floated onto copper grids.
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The amorphous carbon and aluminium specimens were prepared by thermal evaporation using a carbon and aluminium source respectively. Films of ta-C were prepared using a filtered cathodic arc deposition system described elsewhere [38]. The implanted ta-C film was irradiated at 300K with 200 keV Xe ions to a dose of $1 \times 10^{15}$ ions cm$^{-2}$ [34, 39]. Table 3.1 shows the density and $sp^2$ fraction of the carbon samples analysed. The $sp^2$ fraction was calculated using the $1s$ to $\pi^*$ feature on the carbon K edges measured using EELS [40]. All plasmon energies were measured in diffraction mode using a 2mm entrance aperture to the EELS spectrometer, which corresponds to an area of $1.13 \times 10^{-3}$ Å$^{-2}$ in reciprocal space.

3.6 Results of Analysis

Fig(3.7) is an intensity contour plot of the set of experimental data collected for aluminium. This type of graph allows the different scattering processes contributing to the electron energy loss spectrum to be visualised more easily. In fig(3.7) features such as the single and double plasmons, highlighted by lines C and D respectively, are clearly visible. Other multiple scattering possibilities involving $Q = 0$ plasmon scattering events, where an electron loses energy in causing a plasmon excitation and then suffers a change in momentum through an elastic scattering event or vice versa can be seen as a line, B, parallel to the elastic scattering line. Line B extends throughout the data set because of the elastically scattered component in the multiple scattering process. Another line that is visible, line E, is perpendicular to the elastic scattering line B. Line E is also formed from a multiple scattering process, in this case the electron suffers a range of $Q = 0$ plasmon scattering events and then an elastic $Q(111)$ scattering event or vice versa. The multiple scattering process essentially replicates the $Q = 0$ electron energy loss spectrum at $Q(111)$.

A corresponding intensity contour plot is shown for ta-C in fig(3.8). There are obvious similarities and differences between the two plots. Clearly present in the plot of ta-C is the elastic scattering line A, the line of $Q = 0$ plasmon scatter-
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![Intensity contour plot of aluminium. It shows the dispersion of the single and double plasmon, lines C and D respectively. It also shows elastic scattering along line A, a multiple scattering event involving a $Q = 0$ plasmon scattering event, B, and a multiple scattering event involving a $Q(111)$ elastic scattering event, E.](image)

**Figure 3.7:** Intensity contour plot of aluminium. It shows the dispersion of the single and double plasmon, lines C and D respectively. It also shows elastic scattering along line A, a multiple scattering event involving a $Q = 0$ plasmon scattering event, B, and a multiple scattering event involving a $Q(111)$ elastic scattering event, E.

There is an obvious difference in the $Q$ dependence between aluminium and ta-C, as expected due to the differences in their electronic structure. In ta-C the valence electrons are more tightly bound to the nucleus of the atom than in aluminium, where the valence electrons can be approximated by a gas of independent electrons. The effect of the stronger binding force on the valence electrons is to damp the plasma oscillations in the material and to change the $Q$ dependence.

Although fig(3.8) does not show a clear double plasmon excitation, the beginning of a line of double plasmon dispersion is present in the 50-60eV region. The most obvious difference between the fig(3.7) and fig(3.8) is the lack of a line E in fig(3.8). The lack of such a line is due to the disordered atomic structure of the amorphous material.
Figure 3.8: Intensity contour plot of ta-C. It shows the elastic scattering line A, the line of $Q = 0$ plasmon scattering events B and C the single plasmon dispersion line.

3.6.1 Dispersion Measurements

By applying the fitting technique discussed in Section 3.4 to data collected from the materials described in 3.5, single plasmon energies were extracted from within the envelope of intensity in the low loss region and dispersion curves were plotted for each of the materials. These curves are shown in fig(3.9), where the single plasmon excitation energy is plotted as a function of the scattering vector.

Also shown in fig(3.9) is the fit to experimental data obtained using the generalised Lindhard eqn(3.19). The generalised Lindhard equation fits the data for a fixed parameter $r$ up to the cut-off wave vector where the behaviour of the single plasmon excitation varies for the different carbon materials, and decays rapidly for aluminium.
Figure 3.9: Dispersion curves measured for the various carbon solids and aluminium. The data points represented by diamonds were determined by least squares fitting. Generalised dispersion curves obtained by fitting eqn(3.19) to the data are also shown (—).
### Chapter 3: Plasmon Dispersion Analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>$r$</th>
<th>$Q_c (\text{Å}^{-1})$</th>
<th>$Q_f (\text{Å}^{-1})$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>1.95</td>
<td>1.3-1.4</td>
<td>1.23-1.35</td>
<td>1.2</td>
</tr>
<tr>
<td>Ion implanted ta-C</td>
<td>1.55</td>
<td>1.4</td>
<td>2.23</td>
<td>$2 \times 10^4$</td>
</tr>
<tr>
<td>Evaporated a-C</td>
<td>1.55</td>
<td>*</td>
<td>*</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>Glassy carbon</td>
<td>1.47</td>
<td>1.7</td>
<td>1.76</td>
<td>$1 \times 10^5$</td>
</tr>
<tr>
<td>$C_{60}$</td>
<td>1.22</td>
<td>1.5</td>
<td>1.86</td>
<td>$2 \times 10^7$</td>
</tr>
<tr>
<td>ta-C</td>
<td>0.59</td>
<td>1.3</td>
<td>3.03</td>
<td>$9.0 \times 10^{13}$</td>
</tr>
</tbody>
</table>

*Not measured to sufficiently high $Q$ to reach $Q_c$.

**Table 3.2:** Displays the results measured from the dispersion curves in fig(3.9). The value of $r$ has an uncertainty of 0.05.

An understanding of the complicated behaviour of the carbon solids after the cut-off wave vector may be gained by considering the nature of the Fermi surfaces in the different materials, and recalling that it is the transfer of energy from the plasmon to a single electron at the Fermi surface that causes the cut-off wave vector. In aluminium the Fermi surface is a sharp boundary with a spherical shape whereas in the carbon solids the Fermi surface can be quite broad and have a complicated shape and as such the cut-off wave vector for the carbon solids is not as distinct, though it is clearly present.

In table(3.2) the values of $r$ determined from fitting the generalised Lindhard model to the plasmon data, and the cut-off wave vector $Q_c$, are given for each of the materials studied.

It can be seen from table(3.2) that the value of $r$ deviates from a value of 2 for aluminium to less than 1 for ta-C. A value of 2 is consistent with previous reports of plasmon dispersion in aluminium [10] and the Lindhard model. The tendency for $r$ to be less than 2 has also been observed [33]. The result that $r$ decreases with $sp^3$ content is also in agreement with these authors.

It is worth noting that the carbon material with the smallest value of $r$, ta-C, is also the least metal-like in its properties, while the carbon material that is the
most metal-like has the largest value of $r$. This relationship with the properties of the electron population is also reflected in the cut-off wave vector.

3.7 Conclusions

In investigating the plasmon dispersion behaviour in the different carbon solids, the dispersion was found to vary from one material to another, thus showing that the dispersion of the plasmon is sensitive to both the atomic and electronic structure within the material. Which allows the different materials to be characterised by their plasmon dispersion relationships.

Using PDA it is possible to discriminate between the carbon solids in a number of ways. The extent of the departure of the electronic structure of a material from that of a free electron gas can be quantified through the measurement of the value $r$ in eqn(3.19). Materials that are closely approximated by a free electron gas having a value of $r$ close to 2 and those which are less closely approximated by this model having a value less than 2.

Materials can also be distinguished by their individual cut-off wave vectors which relate to the Fermi surface in the solid. Furthermore materials can be discriminated by the rapid decrease of the cut-off wave vector; this contains information about the density of electronic states and shows they are affected by the extent of disorder in the structure.

It is clear that PDA can be used to investigate the electronic structure in materials; however to better understand the experimental results, more theoretical work needs to be done on the phenomenon of plasmon excitation and dispersion in materials that are not well approximated by a free electron gas.
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Chapter 4

Reduced Density Function Analysis using Convergent Electron Illumination

4.1 Introduction

The energy filtered electron diffraction pattern (EFDP) technique developed by Cockayne and McKenzie [1, 2] and discussed in Chapter 2 allows structural information to be obtained from amorphous and polycrystalline materials using high energy electrons. At the time that EFDP was developed it was already possible to obtain this same information using neutrons and X-rays [3, 4, 5]; however the relatively low probability for interaction with a material exhibited by both neutrons and X-rays meant that in many situations (e.g. thin amorphous films used
as hard coatings or for solar collection, amorphised regions in semiconductors, intergranular phases), there was insufficient material present in the specimen to allow these techniques to be used. Thus one motivation for using electrons to perform the analysis was that their relatively high probability for interaction with a material [6] would allow analysis of much smaller volumes of material than was previously possible.

The measurement and conversion of an EFDP, collected in an electron microscope, into a reduced density function, $G(r)$, is now a well established technique [7]. Determination of $G(r)$, as demonstrated in Chapter 2, allows measurement of nearest neighbour distances, to an accuracy of 0.02Å, as well as bond angles and coordination numbers. The technique has been successfully applied to both polycrystalline and amorphous materials [8, 9, 10].

Through EFDP, using electrons, experimentalists now have a means of obtaining structural information from quite small specimen volumes. However for amorphous materials the sample size that can be investigated using EFDP is still relatively large and measurements convey information about the average structural properties of the material. Any attempt to obtain "local" structural information requires the investigation of even smaller specimen volumes. To do this changes have to be made in the way that the electron scattering experiment is executed.

When performing $G(r)$ analysis, measurements of $I(Q)$ are taken in an electron microscope, where $Q$ is the scattering parameter (defined as $Q = 4\pi \sin(\theta)/\lambda$ with $2\theta$ being the scattering angle and $\lambda$ the wavelength of the electrons). The smallest volume that can be analysed is restricted by the requirement that intensity at a point $p$ in the diffraction pattern is derived from a singular scattering parameter $Q$. The requirement is satisfied by employing parallel electron illumination to perform the analysis. An obvious method for reducing the volume illuminated is therefore to reduce the width of the electron beam by introducing smaller collimating apertures. However there are problems with this method. Firstly
using a small aperture reduces the intensity of the illumination, making it difficult to obtain reasonable statistics and thus reducing the range over which $I(Q)$ can be measured. Also the smallest aperture sizes that can be made at present have a diameter of the order of 10$\mu$m which though small, is still large on an atomic scale.

Another method for reducing the volume from which $G(r)$ analysis can be performed is to converge the illumination used; this has two advantages, one being that there is no loss of intensity as the size of the volume illuminated is reduced, and the other is that extremely small volumes can be illuminated. For example, in a scanning transmission electron microscope (STEM), convergent probes can be formed which have probe sizes of less than 1 nm [11]. There is a problem in using convergent illumination though, in that it does not satisfy the requirement for a singular $Q$ to be associated with each point $p$ in the diffraction pattern, see fig (4.1). It is the solution of this problem which forms the subject matter for this Chapter and which will enable the use of convergent illumination in performing $G(r)$ analysis.

\[ \text{Intensity at } p = I(Q_0) \]

\[ \text{Intensity at } p = I(Q_0) + I(Q_1) \]

**Figure 4.1:** Parallel and Convergent illumination. Using parallel illumination, intensity at $p$ is derived from a unique scattering parameter $Q$. When using convergent illumination, intensity at $p$ can be derived from multiple scattering parameters.
Chapter 4: Reduced Density Function Analysis

4.2 The Problem

The use of convergent illumination results in a range of different directions for the incident electrons. If it is assumed that electrons incident upon the specimen in a particular direction are incoherent with electrons of any of the other directions [12, 13], then the observed diffraction pattern can be considered to be the superposition of the diffraction patterns formed from each of the different directions of incidence. This is equivalent to the situation in which the diffraction pattern formed from a single direction of incidence is convolved with a point spread function (PSF). In this case the PSF is the intensity distribution function of the convergent beam and has a width determined by the convergence angle of the convergent beam.

The problem, then, is obtaining \( I(Q) \), the diffraction pattern formed from a single incident direction, from measurements of \( H(Q) \), the convergent beam diffraction pattern, and \( J(Q) \), the PSF. This problem is an inverse problem and can be solved by deconvolution, and its solution will allow \( G(r) \) analysis of smaller specimen volumes.

4.3 Deconvolution

Deconvolution is a standard mathematical operation applied to experimental data to remove blurring or spreading which is present due to the finite resolving power of the instrument used to measure that same data. In the situation where the data is an image (2 dimensional data set) or a spectrum (1 dimensional data set), both of which are routinely measured in a TEM, the extent of the blurring can be determined by the measurement of a point source, as the resulting image or spectrum of this point source is the PSF. This PSF is normally described as the instrumental function or profile and is convolved with the “real” data to give the blurred data that is observed experimentally. In this Chapter it is important to note that deconvolution is not being used to correct for instrumental effects,
Chapter 4: Reduced Density Function Analysis

instead it is being used to “extract” data from the measurements which satisfies the condition that the intensity at a point $p$ is derived from a single scattering parameter $Q$.

Deconvolution is an inverse problem, where the real or idealised data set, hypothetically measured from an instrument of infinite resolution, is obtained by inversion of the observed data set with the PSF. The process of inversion is normally performed in the Fourier domain to take advantage of the fact that inversion in this domain can be effected by simple division of the two measured quantities.

The simplicity of the deconvolution process in the Fourier domain is deceiving, as in experimental situations there is always an additional noise component which contributes to the observed spectrum. In performing the deconvolution the noise is amplified, and errors can be introduced into the estimate of $I(Q)$. In the current situation, attempts to use this procedure showed the errors to be severe. This, coupled with the fact that deconvolution as an inverse problem is also an ill-posed problem (which essentially means that it has no unique solution, see Section 4.4.2), makes deconvolution a difficult task to perform, on top of any difficulties which the experiment itself may present.

Any reasonable deconvolution method must then deal adequately with the problems of noise amplification and of selecting a plausible solution from the family of solutions which when convolved with the PSF will give the observed data within a certain tolerance. Given the complexity of these problems, deconvolution has become an area of study in its own right, resulting in a large variety of different deconvolution methods which are often tailored to particular experimental problems. Jansson has divided these methods into two main categories, “linear methods” and “non-linear constrained methods” [14].

The linear methods include low-pass and Wiener filtering. These methods are linear in that each data element in the deconvolution estimate is a linear combination of the input data elements of the observed spectrum. The non-linear constrained
methods include maximum entropy (ME) and iterative blind deconvolution (IBD) which is based on the Richardson-Lucy algorithm developed independently by Richardson [15] and Lucy [16]. The deconvolution methods mentioned, as well as many others, all allow estimates of $I(Q)$ to be obtained in a variety of different situations. A choice between them is made by deciding which method best suits one’s own experimental situation.

An initial choice not to use linear methods was made because, in general, they overcome the noise amplification problem by excluding high frequency information, and though noise is reduced, there is then no possibility of regaining high frequency information pertaining to the real data.

To determine which of the non-linear methods to employ, the performance of two of the more popular methods, ME and IBD, are compared in two different situations; the first when the PSF is known, the second when the PSF is partially known. Then having selected an appropriate deconvolution technique, $G(r)$ analysis is demonstrated using diffraction patterns measured with convergent electron illumination. The experimental data is obtained from glassy carbon.

4.4 Theory

In this Section a simple mathematical treatment of the basic problems of deconvolution is presented, as a starting point for understanding the more complex non-linear constrained deconvolution methods IBD and ME and the increase in the accuracy of the deconvolution results that can be achieved by applying simple constraints to the allowed solutions. Then the deconvolution algorithms IBD and ME, which are to be tested in Section 4.5, are developed.

4.4.1 Noise and Deconvolution

Consider the ideal situation where experimentally measured data is noise free, in which case the observed data $H(Q)$ is a simple convolution of $I(Q)$ and $J(Q)$,
written as

$$H(Q) = \int_{-\infty}^{\infty} I(x)J(Q - x)dx. \quad (4.1)$$

The Fourier transformation of eqn(4.1) is

$$h(u) = i(u)j(u), \quad (4.2)$$

where $h$, $i$ and $j$ are the Fourier transforms of $H$, $I$, and $J$ respectively. $i(u)$ can then be retrieved by rearrangement of eqn(4.2)

$$i(u) = \frac{h(u)}{j(u)}. \quad (4.3)$$

The inverse Fourier transform of $i(u)$ gives $I(Q)$ and the deconvolution is complete. In reality however there is always noise present in the observed spectrum. To describe this, eqn(4.1) is rewritten with an additional noise component $N(Q)$.

$$H(Q) = \int_{-\infty}^{\infty} I(x)J(Q - x)dx + N(Q). \quad (4.4)$$

The Fourier transformation of eqn(4.4) gives

$$h(u) = i(u)j(u) + n(u). \quad (4.5)$$

Rearrangement of eqn(4.5) gives the result

$$i(u) = \frac{h(u)}{j(u)} - \frac{n(u)}{j(u)}. \quad (4.6)$$

In the situation being considered, $n(u)$ extends to high frequencies whilst $h(u)$ and $j(u)$ decrease with increasing $u$. As a result, using this technique will amplify the high-frequency noise and introduce errors in the estimate of $I(Q)$.

### 4.4.2 An Ill-Posed Problem

It has been mentioned briefly in Section 4.3 that deconvolution is an ill-posed problem in the sense that any solution which is obtained is non-unique. This problem becomes apparent through consideration of the two sets of data

$$H(Q) = \int_{\infty}^{\infty} I(x)J(Q - x)dx, \quad (4.7)$$
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<table>
<thead>
<tr>
<th>$I_a$</th>
<th>1</th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>1</th>
<th>$I_b$</th>
<th>1</th>
<th>1.5</th>
<th>1.5</th>
<th>1</th>
<th>2.5</th>
<th>0.5</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>slide</td>
<td>$J$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>slide</td>
</tr>
<tr>
<td>$H_a$</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td>$H_b$</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Tabular representation of data sets $I_a$ and $I_b$ convolved with the PSF, $J$.

and

$$H'(Q) = \int_{-\infty}^{\infty} [I(x) + O(x)] J(Q - x) dx. \quad (4.8)$$

Then $H(Q) = H'(Q)$ if

$$\int_{-\infty}^{\infty} O(x) J(Q - x) dx = 0. \quad (4.9)$$

Consequently the data $H(Q)$ does not differentiate between $I(x)$ and $I(x) + O(x)$ if $\int O(x) J(Q - x) dx = 0$.

This uniqueness problem can be more clearly understood by considering simple convolutions of two discrete series of numbers, $I_a$ and $I_b$ with a PSF $J$. Let $I_a = \{1,1,2,1,2,1,1\}$ and $I_b = \{1,1.5,1.5,1,2.5,0.5,1\}$. Convolving both with the PSF, $J = \{1,1,1\}$. In its discrete form eqn(4.1) is expressed as

$$H_m = \sum_{n=1}^{N} J_{nm} I_m, \quad (4.10)$$

and thus the two convolutions can be displayed in a tabular form as running averages.

From the calculations in table(4.1) it can be seen that $H_a$ and $H_b$ are identical. Given that the PSF used to generate both observed results is identical any inversion performed is going to be an approximation of the original data set because clearly the result is not unique. How then can the experimentalist be sure that the deconvolution result obtained is a reasonable representation of the real data? To answer this question it is useful to examine the Fourier transform of eqn(4.9).

$$j(u) o(u) = 0 \ \forall u. \quad (4.11)$$
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In a typical experimental situation $j(u)$ is large for small values of $u$ and diminishes as $u$ gets larger. If the relationship in eqn(4.11) is to be satisfied when $j(u)$ is finite $o(u)$ must equal zero. However when $j(u) = 0$, $o(u)$ can take any finite value. Fortunately this situation is restricted to high frequencies, and so treatment of the more serious effect caused by noisy data (described in the next Section) tends also to manage this problem of non-uniqueness.

4.4.3 Constraints

Modern deconvolution methods frequently make use of constraints, to reduce the size of the solution set to any particular problem and thus increase the confidence one has that the result is an accurate representation of the data. They also help to regain frequencies that have been lost in the measuring process due to the finite resolving power of the measuring instrument, (since information is contained implicitly in the constraint) and help to minimise spurious effects induced in the solution due to noise in the measured data.

Constraints implemented in deconvolution algorithms are based on prior knowledge about which solutions are physically possible. One of the most simple yet powerful constraints applied when deconvolving image or spectral data is the constraint of positivity, that is, the solution obtained may not contain any negative values. This type of constraint is an amplitude constraint and in some specific situations more than one amplitude constraint can be applied. For example in some situations it is known that intensity in a spectrum falls between two specific limits. Spatial and frequency constraints can also be applied depending on what knowledge one has about the data. The implementation of constraints in modern methods has led to a marked improvement in the accuracy of deconvolution solutions especially in the presence of noise.
4.4.4 The Richardson-Lucy Algorithm

The Richardson-Lucy algorithm has been applied to the problem of deconvolution in a wide range of fields including confocal microscopy [17] and astronomy [18]. One of the main reasons for its popularity is that it can perform deconvolutions in the presence of quite high levels of noise [19]. In developing this algorithm the standard constraint of positivity is applied, [eqn(4.12)], as well as normalisation of the PSF, [eqn(4.13)].

\[ I(x) \geq 0 \forall x. \quad (4.12) \]

\[ \int_{-\infty}^{\infty} J(x)dx = 1. \quad (4.13) \]

The Richardson-Lucy algorithm is actually based upon Bayes’ theorem [19], which when applied to eqn(4.1) gives \( j(x - Q) \) (the inverse of the convolution kernel \( J(Q - x) \))

\[ j(x - Q) = \frac{J(Q - x)I(x)}{\int_{-\infty}^{\infty} J(Q - x)I(x)dx}. \quad (4.14) \]

Rearrangement of eqn(4.14), making use eqn(4.1) and of the condition that \( J(Q - x) \) must be normalised, gives

\[ I(x) = \int_{-\infty}^{\infty} H(Q)j(x - Q)dQ. \quad (4.15) \]

The form of eqn(4.15) is deceptive, as it suggests that \( I(x) \) is obtainable through straightforward evaluation of eqn(4.15). However this is not possible because \( j(x - Q) \) is a function of \( I(x) \). Another possible approach to obtaining the solution \( I(x) \) that is apparent from eqn(4.15) is through iteration. This iterative approach is the Richardson-Lucy algorithm.

\[ I^{m+1}(x) = I^m(x)\frac{\int_{-\infty}^{\infty} H(Q)j(x - Q)dQ}{H^m(Q)}, \quad (4.16) \]

where \( H^m(Q) \) is defined as

\[ H^m(Q) = \int_{-\infty}^{\infty} J(Q - x)I^m(x)dx. \quad (4.17) \]
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One of the advantages of the Richardson-Lucy algorithm is that it intrinsically accounts for the constraint of positivity, eqn(4.12). As can be seen from eqn(4.16), as long as \( I^0(x) > 0 \), then \( I^m(x) > 0 \).

4.4.5 Iterative Blind Deconvolution Based on the Richardson-Lucy Algorithm

IBD is a numerical method for performing deconvolution when neither \( I(Q) \) nor \( J(Q) \) are known and only the observed data \( H(Q) \) is available; this form of deconvolution is known as blind deconvolution [20]. IBD based on the Richardson-Lucy algorithm allows simultaneous estimation of both the real data and the PSF. The method has been successfully applied by Tsumuraya et al. [21] to deconvolve speckle images and by Holmes and Liu [22] to restore images formed with fluorescence and confocal fluorescence microscopies.

To use the Richardson-Lucy algorithm to perform IBD the PSF must also be estimated. In Section 4.4.4 it was shown that the Richardson-Lucy algorithm is capable of obtaining an estimate for \( I(Q) \). Through a simple change of variable in eqn(4.1) that same method can be applied to form an estimate of \( J(Q) \). If the substitution \( x' = Q - x \) is made in eqn(4.1) the result is

\[
H(Q) = \int_{-\infty}^{\infty} I(Q - x')J(x')dx'.
\]  

(4.18)

Once again making use of Bayes' theorem and the normalisation constraint, which is now applied to \( I(Q - x') \) in eqn(4.18) gives

\[
J(x') = \int_{-\infty}^{\infty} J(Q)i(x' - Q)dQ,
\]  

(4.19)

and

\[
J^{m+1}(x') = J^m(x')\frac{\int_{-\infty}^{\infty} H(Q)I(Q - x')dQ}{H^m(Q)},
\]  

(4.20)

which is analogous to the estimate of \( I(Q) \). However in eqn(4.20) \( H^m(Q) \) is now defined as

\[
H^m(Q) = \int_{-\infty}^{\infty} I(Q - x')J^m(x')dx'.
\]  

(4.21)
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This difference is only superficial as the convolution operation is independent of the order in which the functions are convolved and as such eqn(4.21) is identical to eqn(4.17). Finally eqn(4.20) violates the normalisation constraint (eqn(4.13)) but by renormalising $J^m(x)$ after each successive iteration the problem can be overcome.

IBD is performed by successive applications of both the estimates for the real data and the PSF to the observed data. A simple procedure is to guess the initial values of both the PSF and the real data then to refine the estimate of the PSF using eqn(4.20). Next the real data is refined using eqn(4.16) and the updated PSF, the whole process is then repeated, see fig(4.2).

![Flowchart](image)

**Figure 4.2:** Graphical representation of the procedure for performing IBD using the Richardson-Lucy algorithm.

### 4.4.6 Boundary Effects

In the presentation of the theory so far it has been assumed that the functions $I(Q)$, $J(Q)$ and $H(Q)$ are of infinite extent in $Q$. However the diffraction patterns collected in an electron microscope using the EFDP technique exhibit upper and lower bounds to $Q$ due to the physical impossibility of collecting data beyond these points. At high $Q$ the boundary is determined by the requirement for
reasonable counting statistics and at low $Q$ the boundary is determined by the very intense unscattered electron beam, which saturates, and in extreme cases may damage, the detector. This finite range in $Q$ leads to two types of error at the boundaries which are normally called boundary effects.

Figure 4.3: Intensity spreading in and out of the measured bounds because of the convolution of the feature with the PSF. If not corrected this will introduce error to the deconvolution estimate.

The first boundary effect occurs as a result of intensity inside the bounds spreading outside the bounds due to its convolution with the PSF, see fig(4.3). The intensity outside the bounds obviously cannot be measured and its absence from the measured data will introduce error into the deconvolution estimate. The second effect is the opposite of the first and occurs when intensity due to a feature outside the measured bounds spreads into the bounded region once again due to its convolution with the PSF, fig(4.3). In this case the error induced in the deconvolution estimate is due to extra intensity within the measured bound which is not derived from features within these same bounds.

These effects have been addressed by Tsumuraya et al. [21] through their extensions to Lucy’s algorithm. Tsumuraya’s approach has been adopted here to deal with these boundary problems. To correct for the first effect, the convolution kernels used in the two estimators, eqns(4.16, 4.20), are renormalised at all positions within the boundaries. This means that whenever the convolution kernel overruns one of the boundaries, the portion of the kernel remaining inside the boundaries is normalised. This renormalisation is achieved by the following
correction terms:

\[
P(Q) = \frac{\int_{B} J(x)dx}{\int_{B} J(x - Q)dx},
\]

(4.22)

\[
R(Q) = \frac{\int_{B} I(x)dx}{\int_{B} I(x - Q)dx}.
\]

(4.23)

\(P(Q)\) is the correction term that is applied to the estimate of \(I(Q)\), and \(R(Q)\) is the correction term that is applied to \(J(Q)\). \(B\) indicates that the integration is to be performed over the range delimited by the spectral boundaries. The correction is implemented by multiplication of the correction terms with the respective convolution kernels for the estimators

\[
I_{mod}(Q) = R(Q)I(x - Q),
\]

(4.24)

\[
J_{mod}(Q) = P(Q)J(x - Q).
\]

(4.25)

Using the modified forms of the convolution kernels the new estimates of \(I(Q)\) and \(J(Q)\) are obtained

\[
I^{m+1}(x) = I^m(x)\frac{\int_{B} H(Q)I_{mod}(x - Q)dQ}{H^m(Q)},
\]

(4.26)

\[
J^{m+1}(x') = J^m(x')\frac{\int_{B} H(Q)I_{mod}(x' - Q)dQ}{H^m(Q)}.
\]

(4.27)

To correct for the second effect, Tsumuraya et al. [21] suggested that each effect would act to dampen the other. They proposed that intensity flowing in and out of the boundaries is in equilibrium, and used this premise to determine the following corrections to the estimates of \(H^m(Q)\). For eqn(4.26) the correction is

\[
H^m(Q) = \int_{B} I(Q - x')P(-Q)J(x')dx',
\]

(4.28)
and for eqn(4.27) the correction is

$$H^n(Q) = \int_B J(Q - x') R(-Q) I(x') dx'.$$

The application of these corrections helps to reduce errors in the deconvolution estimate caused by the finite extent of the measured spectrum.

### 4.4.7 Symmetry Constraint

As IBD is simultaneously estimating $J(Q)$ as well as $I(Q)$ it becomes possible to introduce prior knowledge about $J(Q)$ into the deconvolution algorithm. In the situation being considered in this Chapter, it is known that $J(Q)$ is circularly symmetric and so it is useful to constrain the estimate of $J(Q)$ to this symmetry [23]. This constraint is implemented by averaging $J(Q)$ about the point $Q = 0$, $J'(Q) = J'(-Q) = \frac{1}{2} (J(Q) + J(-Q))$ and then using the average as the updated $J(Q)$.

### 4.4.8 Maximum Entropy

The maximum entropy method (like the Richardson-Lucy algorithm) has been applied in a variety of different experimental situations, for example deconvolution of images formed in an electron microscope [24], medical imaging [25], spectra in ion beam experiments [26] and astronomical images [27]. In all these situations deconvolution using ME has substantially increased the resolution over that of the raw experimental data. How then is ME different from the Richardson-Lucy algorithm? The essential difference between ME and the Richardson-Lucy algorithm is that as well as making use of constraints such as positivity, to reduce the size of the set of solutions to the ill-posed problem, ME also seeks the solution, from the reduced solution set, that is most probable.

A standard method for performing deconvolution is to minimise the $\chi^2$ value for the difference between the observed data and the convolution of the PSF with the estimate of the real data, subject to a constraint that incorporates prior
knowledge about the form of the real data, eqn(4.30). In practise this constraint is often one of smoothness and the constrained entropy, \( S \), is then minimised using the standard method of LaGrange multipliers [28].

\[
S = \sum_{n=1}^{N} \frac{1}{\sigma_n^2} \left( \sum_{m=1}^{N} J_{nm} I_n - H_n \right)^2 + \lambda G(I_1, \ldots, I_N). \tag{4.30}
\]

In eqn(4.30) \( \lambda \) is the LaGrange multiplier, \( G \) is the constraint and the term within the summation is the \( \chi^2 \) value. To obtain the ME method from eqn(4.30) the function employed for \( G \) is the Shannon entropy function [14], ie

\[
G(I_1, \ldots, I_n) = \sum_{n=1}^{N} I_n ln(I_n). \tag{4.31}
\]

The entropy function is chosen because it gives the least biased estimate of the most probable solution [29]. Minimising eqn(4.30) after substitution of eqn(4.31) for \( G \) is equivalent to maximising the constrained entropy (hence the name 'maximum entropy').

There are a number of possible numerical methods by which one can obtain the minimum to eqn(4.30). One of the more popular methods was developed by Skilling [30]. However a simple algorithm derived by Kuzuo [31] is chosen for implementation here because of its avoidance of complex and often unstable root finding methods. Kuzuo avoids the root finding problem through use of a user defined constant, \( \lambda \) (LaGrange multiplier) which effects the rate of convergence but does not change the final result. Note that if \( \lambda \) is too large the algorithm may not converge to the desired accuracy as each subsequent iteration bounces back and forth around the actual result.

The Kuzuo algorithm is given by

\[
I_j^{i+1} = I_j^i exp(-1 - \lambda R_j[I^i]), \tag{4.32}
\]

where \( R_j[I^i] \), commonly referred to as the \( \chi^2 \) value, is defined as

\[
R_j[I^i] = \sum_{n}^{N} \left\{ J_{nj} \left( \sum_{k}^{N} J_{nk} I_k - H_n \right) / \sigma_n^2 \right\}. \tag{4.33}
\]
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Given that there are a number of different ME algorithms it is fair to say that the comparison between ME and IBD performed in Section 4.5 is actually between the Kuzuo ME algorithm and Richardson-Lucy IBD.

4.4.9 Calculation of G(r)

Once the diffraction pattern formed with convergent illumination has been deconvolved it will be necessary to calculate \( G(r) \). Recalling the results of Chapter 2, \( G(r) \) is determined for a single atomic species by converting \( I(Q) \) to a reduced elastic scattering intensity \( \Phi(Q) \)

\[
\Phi(Q) = Q \left[ \frac{I(Q) - Nf^2(Q)}{Nf^2(Q)} \right]
\]  

(4.34)

where \( f(Q) \) is the atomic scattering amplitude and \( N \) is a scaling factor. \( \Phi(Q) \) is then converted to a \( G(r) \) by Fourier sine transformation

\[
G(r) = \frac{2}{\pi} \int_B \Phi(Q) \sin(Qr) \, dQ.
\]  

(4.35)

4.5 Testing the Algorithms

In order to test the performance of the ME and IBD deconvolution algorithms and to determine which of the algorithms is more suitable for performing the deconvolution of the convergent beam illuminated diffraction patterns, the two algorithms were tested upon modelled spectral data in two different situations. As previously mentioned in Section 4.3, the first situation is when the PSF is accurately known and the second situation is when the PSF is only partially known.
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Figure 4.4: Model spectrum containing two peaks and comprised of 64 data points, with PSF inset.

Fig(4.4) shows a model spectrum. The spectrum consists of two peaks and is comprised of 64 data points. Inset in fig(4.4) is a typical PSF, also comprised of 64 data points. The PSF is a Gaussian function with a FWHM of \( \approx 10 \) datapoints.

Figure 4.5: The spectrum was formed by the convolution of the model spectrum in fig(4.4) with the inset PSF together with the addition of noise.
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The spectrum in fig(4.5) is formed by the convolution of the spectrum in fig(4.4) with the inset PSF. To simulate experimental conditions noise has also been added to the convolution. The noise is Gaussian in form, having a normal distribution with a standard deviation of 0.2 and a mean of 0.0.

In fig(4.6) two spectra are shown, one is the result of the deconvolution of the spectrum in fig(4.5) with the PSF inset in fig(4.4) using the ME algorithm. The other is the result of the same deconvolution except this time obtained using IBD. As can be seen there is little difference in the results achieved using the two different methods. Both have managed to effectively regain the two peaks that are present in the model spectrum shown in fig(4.4).

![Deconvolution spectra obtained using ME and IBD. Both algorithms produce a similar estimate when the PSF is known.](image)

**Figure 4.6:** Deconvolution spectra obtained using ME and IBD. Both algorithms produce a similar estimate when the PSF is known.

Next the performance of the two algorithms is compared when the PSF is only partially known. To perform this test the shape of the original PSF is distorted, see fig(4.7). The distorted PSF has a FWHM which is $\approx 20$ data points and exhibits a flat top.

The spectra displayed in fig(4.8) are the deconvolution results, using the distorted PSF, obtained using ME and IBD. It can be seen that the ME technique has failed
Figure 4.7: The distorted PSF has a FWHM of $\approx 20$ datapoints and exhibits a flat top. The original PSF is also shown for comparison.

to give a reasonable estimate in this particular situation.

Figure 4.8: Deconvolution spectra obtained using ME and IBD. Even though the deconvolution was performed with a distorted PSF, IBD still produces a reasonable estimate of the original spectrum, however ME does not produce a good deconvolution estimate in this situation.

The reason for this is, that even though ME employs a more sophisticated method
for determining the most probable solution, it is still reliant on a reasonably accurate knowledge of the PSF, as are most deconvolution algorithms. By contrast, IBD has managed to obtain a reasonable deconvolution result despite the distorted PSF, although obviously without the same accuracy that is achievable when the PSF is known.

![Original vs. Reconstructed PSF](image)

**Figure 4.9:** The original PSF and the PSF estimate determined using IBD.

IBD has also produced a reasonable estimate of the original PSF, demonstrating again the effectiveness of IBD in the situation where the PSF is only partially known. In fig(4.9) a comparison of the original PSF and the reconstructed PSF is shown.

### 4.6 Deconvolution of Convergent Beam Electron Diffraction Patterns

In order to demonstrate RDF analysis using convergent electron illumination, electron diffraction patterns were measured from a glassy carbon specimen using the technique of Cockayne and McKenzie [1]. The glassy carbon was supplied by Atomergic Chemets Corp (New York) and the samples were prepared for
viewing in a TEM, in cross section, using ultramicrotomy [32].

Previously collection of electron data in a TEM, using the technique of Cockayne and McKenzie [1], has been performed solely with parallel electron illumination, to satisfy the condition specified in Section 4.1. In this case electron diffraction data were collected with convergent illumination in order to perform RDF analysis from smaller specimen volumes. The illumination was converged using the condenser lens of the TEM.

As well as collecting diffraction data, the PSF of the convergent electron illumination must also be measured so that deconvolution can be performed. To do this, illumination in the diffraction plane was measured, in the absence of a sample, under precisely the same electron-optical configuration as was used to collect the diffraction pattern when the sample was present. However this measurement presents a number of practical problems which affect the accuracy with which the PSF can be measured. This is an important point as highlighted by the failure of ME and the reduced accuracy of the IBD when the distorted PSF was used to perform the deconvolution.

The first problem arises out of the way the diffraction data is collected using the EFDP software. In order for the PSF to be measured along its diameter, collection must begin before illumination in the diffraction plane due to the converged beam starts, and must continue after it has finished, see fig(4.10). As there is no intensity in the outer regions, the peak search algorithm used for controlling the position of the ZLP (see Section 2.2.3) on the photodiode array fails and no measurements can be made. To overcome this difficulty the EFDP program was modified, such that it simply collected intensities, without trying to correct for problems such as the drift of the ZLP. As the region over which the PSF extends is only small, requiring only a short collection time, this is possible, however it does reduce the accuracy of the measurement of the PSF.

A further difficulty that was encountered in measuring the PSF was due to the
Figure 4.10: PSF measured using convergent illumination and attenuation (through the PEELS unit), the PSF is noisy and asymmetrical.

very large intensities of the unscattered electrons. Initially, to give reasonable counting statistics in the electron diffraction pattern the TEM is configured such that the intensity of the incident beam is reasonably high. As the PSF has to be collected under the same configuration the resulting intensity in the PSF is so large that it exceeds the dynamic range of the detector, which then saturates. Remember that the previous method, (see Section 2.3.2), for avoiding difficulties in this region was to simply not measure the intensity!

In order to reduce the intensity in the incident beam the PSF is measured with the attenuator of the PEELS unit activated. This reduction in intensity allows the PSF to be measured. However the attenuation introduces large errors into the height and position of the ZLP, resulting in noise and asymmetry in the PSF measurement, see fig(4.10). To increase the accuracy of this measurement it was repeated several times and the average of these measurements was used as the PSF in the deconvolution process. Note that as the PSF is measured in diffraction mode its shape is determined by the smallest condenser or selected area aperture in place above the specimen, giving the PSF a circular symmetry which can be
used to aid the deconvolution.

The difficulties in measurement of the PSF result in a PSF that is reasonably inaccurate. This being the case it can be expected that IBD, as demonstrated in Section 4.5, will give the better deconvolution estimate. It should be pointed out that this does not mean that IBD is better than ME, it is simply more applicable to this particular situation. As such IBD is used to perform the deconvolution in the subsequent analysis.

Fig(4.11) shows a diffraction pattern of glassy carbon collected with parallel electron illumination. The diffraction pattern does not contain the unscattered electron peak as this peak is too intense to measure; also the diffraction pattern of amorphous glassy carbon exhibits a reasonably diffuse ring structure. This spectrum will be used as a standard with which the deconvolution results can be compared.

Fig(4.12), like fig(4.11), shows a diffraction pattern of glassy carbon except the diffraction pattern in fig(4.12) is collected using convergent electron illumination. The difference between the two figures is clear in that the peaks in fig(4.12) have been blurred due to their convolution with the convergent beam PSF. There is also a significant noise in the peaks at $Q = 0.3$ and $Q = 0.5$; this is most likely due to instabilities in the high tension supply in the TEM, which tend to decrease after the microscope has been in operation for a reasonable period of time, but can be aggravated by different problems such as a decrease in the vacuum pressure.

Fig(4.13) is the deconvolution of fig(4.12) obtained using IBD. The deconvolution has accurately restored the peaks that were first observed in fig(4.11), in terms of peak height and position. The deconvolution has also significantly reduced the noise present in the spectrum when compared with that of fig(4.12). A spurious peak has been formed at $Q = 0.2$ due to the inadequacies of the boundary conditions in dealing with the very intense unscattered electron peak at $Q = 0$. 

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**Figure 4.11:** An electron diffraction pattern of glassy carbon formed using parallel electron illumination.

**Figure 4.12:** The spectrum shows a diffraction pattern of glassy carbon collected using convergent electron illumination. The rings in the spectrum are notably broadened when compared with those in fig(4.11), due to convolution with the convergent beam PSF.

**Figure 4.13:** Deconvolution has largely restored the original glassy carbon diffraction pattern, as well as filtering out a significant noise component.

Finally all three diffraction patterns have been converted to $G(r)$ using eqn(4.34).
and eqn(4.35). From fig(4.14) it can be seen that the deconvoluted diffraction pattern has produced a $G(r)$ which demonstrates a greater similarity to the $G(r)$ of the diffraction pattern formed with parallel illumination then does the $G(r)$ of the diffraction pattern formed with convergent illumination. This similarity makes it clear that it is possible using deconvolution techniques to analyse smaller specimen volumes than is currently possible using standard RDF analysis.

![Graph](image)

**Figure 4.14:** $G(r)$ curves formed from the parallel, converged and deconvolved diffraction data, show that deconvolution of the converged data allows $G(r)$ analysis to be performed using convergent electron illumination. It also demonstrates how it is possible using non-linear deconvolution techniques to regain high frequency information that has been lost due to the finite resolution of the measuring apparatus.

Another interesting feature is observed in fig(4.14) if the $G(r)$ are considered to be the frequency spectra of the different diffraction patterns. This consideration would of course be an exact statement except for the fact $I(Q)$ has had a normalising factor $Nf(Q)^2$ subtracted before it is Fourier transformed to $G(r)$, see eqn(4.35). At large $r$, or high frequency the $G(r)$ formed from the deconvoluted diffraction pattern has regained frequency components lost to the $G(r)$ of the diffraction pattern formed with convergent illumination. The improvement is quite dramatic - in many instances the peaks in the deconvolved $G(r)$ have
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actually changed concavity when compared with those of the convergent $G(r)$. This demonstrates the ability of non-linear deconvolution methods to regain high frequencies lost in the measuring process.

4.7 Discussion

It has been demonstrated in this Chapter that RDF analysis of electron diffraction patterns formed using convergent electron illumination is possible using non-linear deconvolution techniques. This allows smaller specimen volumes to be analysed than is possible using the standard RDF technique which requires the use of parallel illumination. The usefulness of IBD has also been demonstrated in the situation where a full and accurate knowledge of the PSF is not available.

There are however, still differences between the $G(r)$ of the parallel illuminated diffraction pattern and the $G(r)$ of the deconvolved diffraction pattern. It was suggested in Section 4.6 that these differences arise because of the inadequacy of the boundary conditions in dealing with the influx of intensity into the measured spectrum due to the large intensity of the unscattered electron peak at $Q = 0$. Clearly the approximation of equilibrium flow [21] is not adequate in this situation.

To estimate the extent of this effect for inclusion in a correction term, a single spectral measurement needs to include both the unscattered electron peak, and a diffraction peak. This is not possible using the particular system of a GATAN 666 PEELS unit coupled to a TEM, because of the limited dynamic range of the photodiode array. The obvious solution to this problem is to employ a detector with a larger dynamic range, and by doing this a similar problem has been solved using an energy filtering (EF) TEM in conjunction with a slow scan CCD [33]. An even more powerful detection system is formed by an EFTEM and an image plate. The large dynamic range of the image plate allows the unscattered electron peak and a diffraction peak to be measured in a single spectrum, see fig(4.15),

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Figure 4.15: The EFTEM and image plate system has the sensitivity and the dynamic range to be able to measure the unscattered electron peak as well as a series of diffraction peaks from an amorphous carbon sample. The first diffraction peak at $Q = 0.2$ is approximately 20 counts, the unscattered electron peak at $Q = 0.0$ is $\approx 19000$ counts.

even though the unscattered peak is $950 \times$ more intense than the largest diffraction peak. It also allows an accurate measurement of the PSF to be made, see fig(4.16) in comparison with fig(4.10). The solution to both these experimental problems allows more accurate deconvolution results to be obtained. Both fig(4.15) and fig(4.16) were taken on a JEM-2010 FEF using an image plate by Dr Kenji Tsuda of Tanaka Lab. Tohoku University, Japan.

Though the EFTEM image plate system solves many of the experimental problems associated with performing an accurate deconvolution, there is a further problem that must be solved before the deconvolution result can be claimed to be completely valid. The problem arises from the finite probability that an electron may pass through the specimen without being scattered. Previously the central peak in the diffraction pattern has been described as the unscattered electron peak. This description is not strictly true. The peak is actually comprised of two types of electrons- unscattered electrons and forward scattered electrons. In
Figure 4.16: Convergent beam PSF measured using a JEM-2010 FEF and an image plate.

this instance forward scattered electrons are defined as electrons that have suffered only very small or no change in direction upon scattering. As it is only the scattered electrons which form the diffraction pattern, the unscattered electron component is a constant intensity added to the diffraction pattern at very small $Q$.

When performing RDF analysis using parallel illumination, the additive constant of the unscattered electrons is not a problem as data in this region is not used anyway. However when convergent illumination is employed this additive constant is spread out over a range of $Q$ corresponding to the convergence angle. Consequently as larger convergence angles are employed to analyse smaller volumes this constant is spread out over a larger portion of $Q$. As the unscattered intensity cannot be accounted for in the deconvolution estimate the error in any deconvolution performed gets larger as the convergence angle is increased.

To overcome this problem the forward and unscattered components of the peak at very small $Q$ must be estimated. This may be done by fitting the diffraction
pattern formed with parallel illumination at moderate values of $Q$ before the first
diffraction peak, and extrapolating the curve back to $Q = 0$. The excess intensity
associated with unscattered electrons could then be estimated and convolved
with the PSF to determine the contribution of the unscattered electrons to the
convergent beam diffraction pattern, which could then be subtracted out, allowing
the deconvolution estimate to be an even more accurate representation of the
parallel illuminated diffraction pattern.

In applying these corrective measures it is feasible that very accurate RDF anal-
ysis could be performed using convergent electron illumination.
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CHAPTER 5

Structural Analysis of Amorphous Materials using Dark Field Imaging

5.1 Introduction

The determination of the atomic structure of a material allows many of its macroscopic properties to be understood, and for this reason much experimental [1, 2] and theoretical [3] effort has been expended in this endeavour. In crystalline materials the determination of structure has become a standard procedure, due largely to the periodic nature of such materials, where once the most basic structural unit, the unit cell, is known the complete structure of the solid is known. Mathematical descriptions of crystalline solids are then simple arrays of atom
positions in the repeated unit, translated throughout the solid by addition of translation vectors [4], fig(5.1).

**Figure 5.1:** The structure of a crystalline solid is completely determined, once the structure of the unit cell is known. The unit cell is then repeated throughout the solid.

In amorphous materials periodicity, or long range order, is absent; however this does not imply a complete lack of structure within the material. Amorphous materials do exhibit structure over a distance of 0-10Å; this structure is called short range order, and is largely due to bonding arrangements between atoms and their nearest neighbours. In describing the structure of disordered materials mathematically, simple arrays of atom positions can no longer be used, and a description of a more probabilistic nature is required to quantify the short range order. Fortunately using statistical mechanics [5, 6], which takes advantage of the fact that the large number of atoms present in the solid allows accurate determination of averaged properties of a material [7], the average structure exhibited in the region of short range order can be described.

In the canonical ensemble involving a system of \( N \) particles the phase distribution function, which describes both the position \( r^N \), and momenta \( p^N \), of the particles
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is given by \( f_N(r^N, p^N) \), where

\[
f_N(r^N, p^N) = \left( \frac{\Lambda}{\hbar} \right) e^{-\beta K_N(p^N)} e^{-\beta V_N(r^N)} Z_N.
\]

Eqn(5.1) \( \Lambda \) is the de Broglie wavelength, \( \hbar \) is Planck's constant, \( K_N(p^N) \) is the kinetic energy, \( V_N(r^N) \) is the potential energy and \( \beta = \frac{1}{kT} \) where \( k \) is Boltzmann's constant and \( T \) is the temperature. \( Z_N \) is the configurational integral [8] given by

\[
Z_N = \int ... \int e^{-\beta V(r_1, ..., r_N)} \, dr_1 ... dr_N.
\]

Eqn(5.1) is actually the probability that a particle is in the phase space \( \Delta p_1 \Delta r_1 \) at \( p_1 r_1 \), and another particle is in the phase space \( \Delta p_2 \Delta r_2 \) at \( p_2 r_2 \), etc. for all \( N \) particles in the system. Eqn(5.1) can then be separated into distributions involving the momenta of the particles and probability density functions involving the positions of the particles. The probability density functions [9] are defined as

\[
p^N(r_1, ..., r_N) \, dr_1 ... dr_N = \frac{1}{Z_N} e^{-\beta V_N(r_1, ..., r_N)} \, dr_1, ..., r_N.
\]

To determine the probability density function for \( m \) particles, \( p^m, p^N \) eqn(5.3) is integrated over all the coordinates of the \((N - m)\) particles that are left.

\[
p^m(r_1, ..., r_m) = \int ... \int p^N(r_1, ..., r_N) \, dr_{m+1} ... dr_N.
\]

If eqn(5.4) is generalised so that any of the \( N \) particles can be arranged in any of the positions \( \Delta r_1, ..., \Delta r_m \), \( p^m(r_1, ..., r_m) \) must be multiplied by \( \frac{N!}{(N-m)!} \) [10] to include all the different possible configurations of the system. This relationship is then simplified by introducing a dimensionless density correlation function \( g^m(r_1, ..., r_m) \) related to \( p^m \) by

\[
p^m(r_1, ..., r_m) = p_{avg} g^m(r_1, ..., r_m),
\]

where \( p_{avg} \) is just the average density of the system.

Of particular interest in diffraction or scattering experiments performed on amorphous materials is the two particle density correlation function \( g^2(r_1, r_2) \). Which

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is simply the probability that there is a particle in $\Delta r_2$ at $r_2$ given that there is already a particle in $\Delta r_1$ at $r_1$. Amorphous materials are homogenous and isotropic, which allows spherical averaging, and $g^2(r_1, r_2)$ depends only on $r = |r_1 - r_2|$, now written as $g(r)$. Eqn(5.5) can then be rewritten as

$$g(r) = \frac{p(r)}{p_{avg}}.$$  \hspace{1cm} (5.6)

This is an important result because it is now clear that the reduced density function $G(r) = 4\pi r(p(r) - p_{avg})$, is actually a form of the two particle density correlation function developed from the statistical mechanics of an $N$ particle system. That is

$$G(r) = 4\pi r(p(r) - p_{avg}) = 4\pi rp_{avg}(g(r) - 1).$$  \hspace{1cm} (5.7)

So in measuring the $G(r)$ of a material one is actually measuring the two particle density correlation function of the material.

The short range order in amorphous materials can be quantified, through experimental measurement of $g(r)$, and materials with different short range order can be differentiated. However from eqn(5.5) it can be seen that $g(r)$ is only one member of a family of density correlation functions which describe the structure in a material and in principle all of these functions must be known before the structure of a material is completely determined.

When investigating amorphous materials a standard procedure used for structural determination is the comparison and refinement of models developed using physical principles with structural information that is determined experimentally, $g(r)$ [11, 12]. Often the situation arises where a number of different structural models compare favourably with the experimental data, and the better model, in the sense that it more accurately represents the “true” structure of the material, cannot be determined. This problem is often described as a uniqueness problem, because the theoretical structure which fits the experimental data is non-unique. Obviously the answer to this problem is to gather more information about the
structure experimentally [13]. However at this point another problem is encountered, for even though scattering experiments give accurate information about $g(r)$, they do not readily give information about any of the other members of the family of density correlation functions [13], which could be used to overcome the problem of uniqueness. Hence work is needed to develop experimental techniques that will allow the measurement of other members of the family of density correlation functions to solve the uniqueness problem.

The reason for the restriction of the experimental data to the determination of $g(r)$ can be understood by investigating the manner in which the intensity $I(Q)$, where $Q$ is the magnitude of the scattering vector $Q$, observed in the diffraction pattern is derived from the specimen. Consider a model of an amorphous material which is built from a basic structural unit. The amorphous material can then be conceived as being comprised of repeated units of this structure but arranged with a variety of different orientations. An accurate model for the derivation of the intensity in the diffraction pattern $I(Q)$ is the Debye model [14] which assumes that $I(Q)$ is the sum of the intensities scattered from each of the different orientations of the basic structural unit, see fig(5.2). $I(Q)$ is then an average measurement in which information about the individual structural units has been lost, which restricts it to the determination of $g(r)$.

If however this intensity could be broken up into the intensity contributions, $I_A(Q), I_B(Q)$ and $I_C(Q)$, from the different orientations then quantities in addition to the mean intensity could be measured and functions dependent on other density correlations besides the pair correlation could be determined.

There are two ways in which it may be possible to obtain such information experimentally in a TEM. One is by illuminating such a small volume of the sample that only a few of the amorphous structural units, shown in fig(5.2), contribute to the scattering process by which intensity is formed in the diffraction pattern. This form of diffraction analysis is called microdiffraction and is normally used
Figure 5.2: Volumes A, B and C represent different orientations of the same basic amorphous structural unit. The intensity at position $Q$ in the diffraction pattern from this simple specimen is then, using the Debye model, the sum of the intensities scattered from each of the different volumes. Note the difference in scattering directions is exaggerated by the scale of the diagram, in reality there is no discernible difference between these directions.

in crystalline structure analysis [15]. Using this technique to study amorphous materials presents a number of difficulties. One is that, microdiffraction patterns formed from nanometre sized regions of the specimen are sensitive to instrumental parameters such as focus and spherical aberration [15]. Therefore the effects of these parameters on the microdiffraction pattern must be quantified before the microdiffraction pattern can be interpreted. Furthermore the microdiffraction patterns are complicated by statistical noise and it is likely that a large number will need to be analysed [16]. Though this procedure is possible it would be time intensive in both the data measurement and processing stages.

The other way in which the information required could be obtained experimentally is through dark field imaging, see fig(5.3), as was shown in early work by Howie and Rudee [17, 18]. A dark field image is formed using scattered electrons, selected by an aperture located in the back focal plane of the objective lens. Using dark field imaging it is possible to separate the diffracted intensity, through spatial resolution, into its constituent parts. This allows functions dependent on higher order correlations to be measured. It also avoids some of the difficulties involved in extracting the same information using microdiffraction, as
a sufficiently large area of the sample may be imaged so that repeated sampling is not necessary.

Recently work by Gibson and Treacy [19, 20, 21, 22], using the technique of "Variable Coherence Microscopy", has shown that information concerning higher order density correlation functions in amorphous materials can be obtained from images collected in a TEM. To perform variable coherence microscopy, a series of hollow cone dark field images are taken using different inner semiangles, and the normalised intensity variance is then plotted as a function of the hollow cone inner semiangle. Using this technique Treacy and Gibson have found evidence for medium range order in amorphous germanium [20].

In this Chapter, work on the feasibility of using dark field imaging techniques, to extract information pertaining to density correlation functions other than the two particle density correlation function \( g^2(r_1, r_2) \), which is measurable using standard diffraction techniques, is presented. It is also the aim of this work to show that such functions are sensitive to short range order and that they are able to contribute to solving the uniqueness problem.
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For this study a dark field imaging method, that is closely related to the method of Treacy and Gibson, is proposed in which the variance of the diffracted intensity is measured as a function of \( Q \). This method is performed by taking a series of dark field images with different scattering angles, and measuring the variance in intensity in each of the images. The feasibility of the method is tested by application to images simulated from known structural models. To perform the simulation the high resolution transmission electron microscope module (HRTEM) of Cerius 2 version 6.1 was used. The structural models used exhibit similar \( G(r) \) functions and the information obtained using the dark field imaging method is then used to discriminate between them. Also the results from these tests allow the determination of the conditions required to apply this method in a TEM; this is done with a view to testing sophisticated models developed by \textit{ab initio} quantum mechanical methods.

5.2 Theory

The proposed technique utilises tilted dark field imaging to access information pertaining to density correlation functions other than the pair correlation function. To understand the technique it is important to realise that the dark field image is interpreted as a map of spatially resolved electron scattering sources, rather than an image of the specimen. In this sense the technique is a hybrid of an electron scattering technique and an electron imaging technique.

By using tilted illumination, an objective aperture centred on the optic axis can be used to form a dark field image. Obviously to obtain good \( Q \) resolution, as is required for an electron scattering experiment, a small \( \Delta Q \) must be used. However if the \( \Delta Q \) used is too small the loss of resolution in the image plane \( \Delta \mathbf{r} \), where \( \mathbf{r} \) corresponds to a vector lying in the plane of the specimen, will be so great that the intensity derived from individual scattering volumes, see Fig(5.2), will not be able to be resolved, and measurement of intensity in the image will only correspond to the mean intensity which is already measurable in the diffraction.

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plane. Clearly to use dark field imaging as a technique for determining individual contributions to the scattered intensity in the diffraction plane will require a delicate balance between $\Delta Q$ and $\Delta \bar{r}$. As the theory is actually dependent on an imaging method, the theory will be presented from this perspective, rather than beginning with some form of the Debye equation which is more standard for scattering experiments.

### 5.2.1 Dark Field Image Intensity

Consider the formation of a tilted dark field image from an amorphous specimen. The amorphous specimen can be considered to be an array of positions $\mathbf{r}_j$ representing atom centres. The specimen is illuminated by a plane wave of incident direction $\mathbf{q}$ with scattered waves $\mathbf{q}'$ that contribute to the dark field image being selected by an objective aperture that is centred on the optic axis. To describe the interaction between the specimen and the electron beam kinematic scattering theory is used [16, 23, 24], and because the spatial resolution required is only moderate and the image is formed from electrons scattered on axis, microscope aberrations are not included [20, 25].

Following arguments similar to those of Treacy and Gibson the wave amplitude of a coherently scattered electron is

$$
\Psi(|\mathbf{q} - \mathbf{q}'|) = i \lambda \sum_j f_j(|\mathbf{q} - \mathbf{q}'|) \, e^{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{r}_j},
$$

where $f_j(|\mathbf{q} - \mathbf{q}'|)$ is the atomic scattering factor and $\lambda$ is the electron wavelength. The dark field image wavefunction is then the Fourier transform of the scattered wave amplitude that is transmitted by the objective aperture, $\psi(\bar{r}, \mathbf{Q})$.

$$
\psi(\bar{r}, \mathbf{Q}) = i \lambda \sum_j \int_{\text{obj}} f_j(|\mathbf{q} - \mathbf{q}'|) \, e^{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{r}_j} \, e^{-i(\mathbf{q} - \mathbf{q}') \cdot \bar{r}} \, d^2 \mathbf{q}'
$$

$$
= i \lambda \sum_j \int_{\text{obj}} f_j(|\mathbf{q} - \mathbf{q}'|) \, e^{-i(\mathbf{q} - \mathbf{q}') \cdot (\bar{r} - \mathbf{r}_j)} \, d^2 \mathbf{q}'.
$$

In eqn(5.9), $\bar{r}$ is the position vector in the image, $\bar{r}$ is equal to $\mathbf{r}$ the position on the surface of the specimen if no magnification is employed and is proportional to $\mathbf{r}$.
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when the image is magnified. \( Q \) is the mean scattering vector that is transmitted by the objective aperture. The integration in eqn(5.9) can be simplified through the use of a change of variable, \( k = q' - q' \), where \( k \) is oriented approximately in the plane of the objective aperture. Using this change of variable the integration in eqn(5.9) can be performed between the limits defined by the reciprocal space radius of the objective aperture.

\[
\psi(\tilde{r}, Q) = i \lambda \sum_j \int_{\text{obj}} f_j(|q - q'|) e^{i(q-q'+q'-q'\cdot \tilde{r} - r_j)} d^2 q' = i \lambda \sum_j e^{-i(q-q\cdot \tilde{r} - r_j)} \int_{\text{obj}} f_j(|q - q'|) e^{i k \cdot \tilde{r} - r_j} d^2 k. \tag{5.10}
\]

As the objective aperture used is reasonably small it may be assumed that the atomic scattering factor \( f_j(|q - q'|) \) does not deviate significantly from \( f_j(Q) \) across the aperture and as such \( f_j(|q - q'|) \) may be replaced by \( f_j(Q) \) in eqn(5.10) which becomes

\[
\psi(\tilde{r}, Q) = i \lambda \sum_j e^{-iQ \cdot \tilde{r} - r_j} f_j(Q) \int_{\text{obj}} e^{i k \cdot \tilde{r} - r_j} d^2 k. \tag{5.11}
\]

The double integral in eqn(5.11) can be evaluated when it is realised that due to the circular symmetry of the problem this integral is in fact in the standard form of an Airy distribution function \[26\].

\[
a_j(\tilde{r} - r_j) = \int_{\text{obj}} e^{i k \cdot \tilde{r} - r_j} d^2 k
\]

\[
a_j(\tilde{r} - r_j) = \pi k^2 A_j
\]

\[
A_j = 2 \times \frac{J_1(K|\tilde{r} - r_j|)}{K|\tilde{r} - r_j|}. \tag{5.12}
\]

In eqn(5.12) \( K \) is the radius of the objective aperture in reciprocal space and \( J_1(K|\tilde{r} - r_j|) \) is a first order Bessel function. A further simplification can be made to eqn(5.12) by setting \( r_j = \sigma_j + z_j \), where \( \sigma_j \) is perpendicular to the optic axis and \( z_j \) is parallel to the optic axis. Using this substitution it is apparent that within the approximation \( k \cdot z_j = 0 \), \( A_j \) is given by

\[
A_j = 2 \times \frac{J_1(K|\tilde{r} - \sigma_j|)}{K|\tilde{r} - \sigma_j|}. \tag{5.13}
\]
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The final form of the dark field wavefunction is

\[ \psi(\vec{r}, Q) = i\lambda \sum_j f_j(Q) e^{-iQ_{ij}(\vec{r}-\vec{r}_j)} a(\vec{r} - \sigma_j). \] (5.14)

Using eqn(5.14) the intensity at a position \( \vec{r} \) in the dark field image wavefunction can be determined from the standard relationship, \( I(\vec{r}, Q) = \psi(\vec{r}, Q)\psi^*(\vec{r}, Q) \), in which the dark field image is multiplied by its complex conjugate.

\[ I(\vec{r}, Q) = \lambda^2 f^2(Q) \sum_i \sum_j a_i(\vec{r} - \sigma_i) a_j(\vec{r} - \sigma_j) e^{-iQ_{ij}r_{ij}}. \] (5.15)

### 5.2.2 Columnar Volume

Given the general form for intensity in a dark field image, eqn(5.15), it is now possible to consider the intensity at a point \( \vec{r} \) in the image. At \( \vec{r} \), the major contribution to the intensity that is measured will be from scattering by atoms which fall within an envelope defined by the central maximum of the Airy function. Atoms outside the envelope will not form a significant contribution to the intensity because of the rapidly decaying and oscillatory nature of the Airy function.

![Graph showing intensity vs. objective aperture size](image)

**Figure 5.4:** Shows the intensity at the point \( \vec{r} = 0 \), when \( Q = 0 \), evaluated from a 125 atom carbon model using eqn(5.15) to give the exact result and using the step function substitution in eqn(5.15) to give the approximate result.
To demonstrate this effect, the intensity at the point $\mathbf{r} = 0$, derived from a 125 atom carbon model, is evaluated using eqn(5.15) when $Q = 0$. This evaluation is then repeated for different objective aperture sizes and the result is plotted in fig(5.4).

In fig(5.4) the intensity rises initially until it reaches a maximum and then decays, as the objective aperture size continues to increase. Initially one would expect that the intensity would continue to increase as the objective aperture size increases until a maximum value for the intensity was reached, the maximum value arising as a consequence of the finite number of atoms in the model. Why then does the intensity decrease? The decrease is due to the fact that as the objective aperture size increases, the width of the central maximum of the Airy function decreases reducing the number of atoms which can contribute to the intensity at $\mathbf{r} = 0$.

Fig(5.5) shows the atoms which effectively contribute to the intensity for the different objective aperture sizes. The decision as to which atoms are effective has been made by including atoms, for which $|\mathbf{r} - \sigma_i| < r_{fwhm}$, where $r_{fwhm}$ is the full width half maximum of the Airy function in eqn(5.15). In this way the Airy function defines a columnar volume within the sample with the approximate dimensions of $\pi r_{fwhm}^2$ multiplied by the specimen thickness from which the intensity at the point $\mathbf{r}$ is derived.

Next consider the intensity measured in an imaging pixel centred on a point $\mathbf{r}$ in the image and whose length and width is $d$. If $d \gg r_{fwhm}$ intensity in the pixel will be derived from a number of different columnar volumes, however if $d \leq r_{fwhm}$ the majority of the intensity in the imaging pixel will be derived from scattering by atoms in a single columnar volume, see fig(5.6). Each pixel in a dark field image sampled in this manner is then comprised of intensity derived from separate columnar volumes which sample the bulk of the specimen. It is worth noting that as the width of the Airy function is controlled by the reciprocal
Figure 5.5: Shows the reduction in the number of atoms contributing to the intensity at the point \( \vec{r} = 0 \) as the objective aperture radius increases.

space radius of the objective aperture, the size of the columnar volume can be varied by changing the size of the objective aperture.
Figure 5.6: This diagram illustrates how intensity in an imaging pixel, whose length and width \( d \leq r_{fwhm} \), derives from a single columnar volume. This diagram also shows the composition of the vectors used in the development of the theory.

The determination of the intensity present in the imaging pixel can be simplified by approximating the Airy function in eqn(5.15) by a top hat function of width \( r_{fwhm} \),

\[
a_i(\mathbf{r} - \sigma_i) = \begin{cases} \frac{B K}{2} & 0 \leq |\mathbf{r} - \sigma_i| \leq r_{fwhm} \\ 0 & |\mathbf{r} - \sigma_i| > r_{fwhm} \end{cases}
\]

(5.16)

The step function has a width \( r_{fwhm} \), and is weighted by a constant \( B \) such that the area underneath the step function is equal to the area underneath the Airy function out to the limit \( r_{fwhm} \). The calculation of the intensity at \( \mathbf{r} \) has been repeated using a modified form of eqn(5.15) in which the step function has
been substituted for the Airy function, the result is also shown in fig(5.4). The similarity between the approximate and exact curves confirms the validity of the approximation.

Through use of the step function approximation, in which the constants $BK$ have been set to equal $C$, the intensity in an imaging pixel corresponding to a particular columnar volume is given by

$$I_{pixel}(Q) = C^2 \lambda^2 f^2(Q) \sum_a \sum_b e^{iQ \cdot r_{ab}}$$  \hspace{1cm} (5.17)

In eqn(5.17) the subscripts $a$ and $b$ represent atoms that fall within the columnar volume defined by the step function.

### 5.2.3 Dark Field Image Statistics

Using eqn(5.17), the mean intensity in the dark field image, $I_{image}(Q)$, can be obtained by summing the intensities from each of the pixels in the image and dividing by the number of pixels, $M$.

$$I_{image}(Q) = \frac{I_{pixel_1} + I_{pixel_2} + \ldots}{M}$$  \hspace{1cm} (5.18)

Substituting eqn(5.17) into eqn(5.18) gives

$$I_{image}(Q) = C^2 \lambda^2 f^2(Q) \left[ \sum_a \sum_b \frac{e^{iQ \cdot r_{ab}}}{M} + \sum_c \sum_d e^{iQ \cdot r_{cd}} + \ldots \right].$$  \hspace{1cm} (5.19)

By choosing an objective aperture of appropriate size $K$ (in eqn(5.12)), the columnar volume may be made small enough to sample a subset of the atomic configurations in the bulk of the specimen. As an amorphous material is both homogenous and isotropic [14], the array of atoms defined by each individual columnar volume may be considered to be different orientations of the same basic array. This means that any vector $r_{ab}$, in the basic array, can have a significant number of different orientations in space with respect to $Q$. If $M$ is large $r_{ab}$ will trace out a sphere of radius $r_{ab}$, see fig(5.7), and the bracketed term in eqn(5.19) can be replaced by $<e^{iQ \cdot r_{ab}}>_{\theta, \phi}$.
Figure 5.7: This diagram shows how the vector \( r_{ab} \), traces out a sphere of radius \( r_{ab} \), when it takes different orientations with respect to \( Q \).

\[
< e^{iQ \cdot r_{ab}} >_{\theta,\phi} = \frac{1}{4\pi r_{ab}^2} \int_{r_{ab}}^{\pi} e^{iQ \cdot r_{ab} \cos(\theta)} r_{ab}^2 \sin(\theta) d\theta
= \frac{\sin(Q r_{ab})}{Q r_{ab}}. \tag{5.20}
\]

Substitution of eqn(5.20) into eqn(5.19) gives

\[
I_{image}(Q) = C^2 \lambda^2 f^2(Q) \sum_a \sum_b \frac{\sin(Q r_{ab})}{Q r_{ab}}. \tag{5.21}
\]

This result is achieved by balancing the simultaneous requirements for both angular and spatial resolution. If the angular resolution is too high the spatial resolution will be poor and will not allow small enough columnar volumes to be formed. Alternatively, the use of high spatial resolution to form quite small columnar volumes requires a loss of angular resolution. Hence there is a need for fine control over the size of the objective aperture to control both spatial and angular resolution.

5.2.4 Debye Equation

As a consequence of using a small objective aperture to obtain reasonable angular resolution \( I_{image}(Q) \approx I(Q) \). This is seen by comparing eqn(5.21) with the Debye
scattering equation, eqn (5.22).

\[ I(Q) = \sum_i \sum_j f_i(Q) f_j(Q) \frac{\sin(Q r_{ij})}{Q r_{ij}}. \]  

(5.22)

As such \( I_{\text{image}}(Q) \) can be converted to \( \Phi(Q) \) in the usual way.

\[ \Phi(Q) = Q \left[ \frac{I_{\text{image}}(Q)}{N f(Q)^2} - 1 \right], \]

(5.23)

where \( N \) is the number of atoms being illuminated by the incident electron beam and \( f(Q) \) is the atomic scattering factor. \( \Phi(Q) \) is the function which through Fourier inversion is converted to \( g(r) \). Consequently \( \Phi(Q) \) is dependent on pair correlations within the material.

5.2.5 Accessing Higher Order Density Correlation Functions

It has been shown in the introduction, 5.1, that the mean diffracted intensity, which is what one observes directly in the diffraction pattern, can only give information about the two particle density correlation function. However now that it is possible to break up the intensity into its constituents other quantities besides the mean intensity can be determined.

Using the same methodology employed as in Section 5.2.3 it is possible to determine the mean of the square of the intensity scattered to a particular \( Q \), by measuring the mean of the square of the intensity in the dark field image \( I_{\text{image}}^2(Q) \).

\[ I_{\text{image}}^2(Q) = B^4 \lambda^4 f^4(Q) \sum_a \sum_b \sum_c \sum_d \frac{\sin(Q(r_{ab} + r_{cd}))}{Q(r_{ab} + r_{cd})}. \]

(5.24)

Through inspection of eqn (5.24) it can be seen that the mean of the square of the intensity in the dark field image is dependent on the atom pairs \( ab \) and \( cd \), whereas the mean intensity in the dark field image is only dependent on a single atomic pair \( ab \), see eqn (5.21). The dependence of eqn (5.24) on the extra atomic pair \( cd \), makes eqn (5.24) sensitive to a higher order correlation function. Thus
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through measurement of eqn(5.24), structural information not available using standard diffraction techniques is revealed.

It is possible to measure eqn(5.24) directly from a dark field image. However it is difficult to tell from inspection of the measurement whether additional structural information is actually present in the dark field image. To do this, eqn(5.24) must be compared with eqn(5.21), which can be done through measurement of the normalised variance in the dark field image [21].

\[ V(Q) = \frac{I_{\text{image}}^2(Q)}{(I_{\text{image}}(Q))^2} - 1. \] (5.25)

\( V(Q) \) is a useful function to measure because, assuming there is no noise or other artefacts in the image, it will only deviate from zero if there is additional structural information present in the image, that is not already revealed by the mean of the diffracted intensity.

By following Gibson and Treacy in measuring intensity statistics from dark field images the proposed tilted dark field technique appears at first glance, to be quite similar to variable coherence microscopy. The difference between the techniques lies in the type of dark field image analysed; variable coherence microscopy uses a hollow cone dark field image as opposed to a tilted dark field image. How then are these two image types different?

Through inspection of eqn(5.15) it can be seen that when there is a spread in the illumination angles, as in hollow cone illumination, the phase terms \( \exp^{-iQr_{ij}} \) for atoms with large \( Qr_{ij} \) are uncorrelated and tend to average to zero. However the phase terms for atoms in which \( Qr_{ij} \) is small are still correlated and these atoms may interfere coherently [19, 27]. Thus through the use of hollow cone illumination, Gibson and Treacy control the degree of coherence in the dark field image, hence the title variable coherence microscopy, which they then use to probe the structure of amorphous materials.

Following the same argument, a tilted dark field image formed using parallel
illumination is a coherent dark field image [16]. Thus unlike variable coherence microscopy the technique proposed in this Chapter does not seek to vary the coherence to probe structure. Instead the image pixel is used to sample atomic configurations from within the corresponding specimen volume.

5.3 Theory Testing

The normalised intensity variance of dark field images has been demonstrated to be particularly sensitive to medium range order [21]. However this does not mean that it is insensitive to variations in short range order. In the theory developed \( V(Q) \) is used to investigate the short range order in amorphous materials. In this Section the sensitivity of \( V(Q) \) to variations in short range order will be tested.

To demonstrate the sensitivity of \( V(Q) \) to short range order eqns(5.21,5.24) were used to calculate \( V(Q) \) from each member of a set of planar polygons. The set contained 5 polygons each having a different number of atoms ranging from 3-7. To ensure that sensitivity to short range order was demonstrated the distance from any atom to the centre of the polygon in each member of the set was fixed at 1.5Å. The results are shown in fig(5.8).

In fig(5.8), all curves are plotted against the same vertical scale and it can be seen that even though the polygons containing 6-7 atoms are very similar structures, they are still clearly differentiated by the function \( V(Q) \), this differentiation being possible through inspection of height, position and number of peaks present in the different plots.

5.4 Model Development

To evaluate whether or not the proposed tilted dark field method is capable of obtaining structural information, not available through more standard techniques, the method is applied to two amorphous carbon models A1 and B1. These models were chosen because they have very similar \( G(r) \) curves and as such
Figure 5.8: $V(Q)$ curves for the set of polygons. The curves clearly differentiate between the different structures, through differences in peak number, height and position. All curves are plotted against the same vertical scale.

are non-unique structures when compared using two particle density correlation information. However the structural composition of the two models is known, and differences in structure are present. If the tilted dark field method is sensitive to a pair-pair density correlation function, the differences in structure between the models should be detected and the $V(Q)$ measured should exhibit this difference.

Both models were prepared, by D.G. McCulloch, using Car-Parrinello molecular dynamics (CPMD) [28, 29] which is a molecular simulation program based on density functional theory. Model A1 has 125 carbon atoms within a cube which
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has a 10.758Å side length. It has a density of 2.0g/cc and is comprised of 80% sp2 and 20% sp3 bonds, see fig(5.9). Model B1 has 64 carbon atoms within a cube which has a 7.596Å side length. It has a density of 2.9g/cc and is comprised of 40% sp2 and 60% sp3 bonds, see fig(5.9).

![Model A1](image1.png)  ![Model B1](image2.png)

**Figure 5.9:** Model A1 is a 125 atom amorphous carbon network. Model B1 is a 64 atom amorphous carbon network.

Comparison of the $G(r)$ curves of the two amorphous carbon models shows that they are both typical amorphous carbon networks with first and second nearest neighbour distances of approximately 1.5Å and 2.5Å respectively, fig(5.10). The similarity between the $G(r)$ curves highlights the fact that a comparison based on two particle correlation information is not sufficient to distinguish the two models.

At present the two models are too small to perform realistic HRTEM simulations on Cerius, which requires atomic networks of approximately 9000 atoms for accurate simulation. However calculating models of such size in an ab initio fashion presents a problem in the large amount of time required to build a model. To
Figure 5.10: $G(r)$ curves of amorphous models A1 and B1 displaying typical nearest neighbour distances for amorphous carbon. The similarity between the curves demonstrates the difficulty in distinguishing similar amorphous structures using pair correlation information.

To overcome this problem, larger models were formed from the two smaller models. The orientations of the smaller models were repeatedly varied in a random manner with the different orientations of the smaller models then being used as building blocks for the larger models.

Model A2 comprised of 9000 carbon atoms, with boundaries of 64.548Å in the $x - y$ directions and 21.516Å in the $z$ direction was built from model A1, and is shown in fig(5.11). Similarly a 8183 carbon atom model, B2, was built from model B1 with boundaries of 45.576Å in the $x - y$ directions and 22.788Å in the $z$ direction.
Figure 5.11: Model A2, a 9000 atom amorphous carbon network, built from randomly oriented units of model A1.

Building the larger models in this manner has the potential to create unphysical situations such as atoms which overlap, and large voids in the material. However comparison of the $G(r)$ curve from the larger model with the $G(r)$ from the smaller model, see fig(5.12), shows that at least from the point of view of $G(r)$ the larger model is an accurate representation of the smaller.
Figure 5.12: $G(r)$ curves of amorphous models A1 and the larger atomic network built from A1 and labelled A2. The similarity suggests that A2 is not greatly affected by the building process and is a good representation of model A1.

5.5 Simulation of the Tilted Dark Field Method

Through the use of the HRTEM module of Cerius tilted dark field images have been formed from the amorphous carbon models A2 and B2. The module allows control over microscope features including beam energy, defocus and spherical aberration so that the simulation environment can be tailored. For these simulations the environment was matched to that of a Phillips EM430 operating at 300kV.

To simulate an image, Cerius employs a multislice method which for reasons of versatility is broken up into three separate steps. First the model is divided up into a number of thin slices, perpendicular to the incident beam direction, the models themselves were oriented such that their z axis was parallel to the incident beam direction. As the simulation is of an amorphous material a much larger number of slices is employed than for a crystalline material of similar thickness [16]. Then using the multislice method of Cowley and Moodie [30, 31, 32, 33],

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the diffraction pattern is calculated for a particular incident beam direction, see fig(5.13).

![Diffraction Pattern Image]

**Figure 5.13:** This image of an amorphous carbon diffraction pattern was generated by Cerius from the 9000 atom amorphous carbon network, Model A2. The image was simulated using a 300kV accelerating voltage.

Finally an image is formed by calculation of the Fourier transform of a portion of the diffraction pattern which is selected by the position and size of the objective aperture, fig(5.14). Clearly the image needs to be formed from a reasonably large specimen to obtain reasonable statistics for the measurement of $V(Q)$ and to more accurately represent a real sample. Hence the need for large models, as mentioned in Section 5.4.

To simulate the tilted dark field method using Cerius, a series of dark field images were formed from the diffraction pattern shown in fig(5.13). The mean $Q$ values used to form each separate image extend along a radius of the diffraction pattern.

A simple test of both the tilted dark field method and the ability of Cerius to perform multislice calculations on amorphous materials was carried out by
Figure 5.14: A simulated dark field image of Model A2 generated using the titled dark field method. The pixel size in this image is $2.69 \times 2.69 \, \text{Å}$. A series of these images measured from different scattering angles is used to determine $I_{\text{image}}(Q)$ and $V(Q)$.

Comparing the mean intensity in each of the dark field images, $I_{\text{image}}(Q)$, with intensity at identical $Q$ values determined by application of the Debye equation eqn(5.22) to model A2.

For comparative purposes $I_{\text{image}}(Q)$ was first converted to $\Phi_{\text{sim}}(Q)$ using eqn(5.23), (the subscript \textit{sim} (meaning "simulated") is to allow differentiation between the Debye measurement of the same quantity). Then $\Phi_{\text{debye}}(Q)$ was determined from model A2 using the Debye equation. This data was convolved over the range of $Q$ accepted by the objective aperture for more accurate comparison. The two curves are shown in fig(5.15).

The similarity in the relative heights and positions of the peaks, of which there are two, one at $0.3 \, \text{Å}^{-1}$ and the other at $0.9 \, \text{Å}^{-1}$ with the peak at $0.9 \, \text{Å}^{-1}$ having the greater height, demonstrated that Cerius is capable of performing the amorphous dark field simulation. It is noticeable that $\Phi_{\text{sim}}(Q)$ is quite noisy when compared with $\Phi_{\text{debye}}(Q)$. This is because, even though the model A2 contains a
Figure 5.15: Comparison of the $\Phi_{\text{sim}}(Q)$ and $\Phi_{\text{debye}}(Q)$. $\Phi_{\text{sim}}(Q)$ is measured from model A2 using the tilted dark field method, simulated on Cerius. $\Phi_{\text{debye}}(Q)$ is determined by application of the Debye scattering equation to model A2.

A large number of different orientations of A1, this number is finite, whereas the assumption intrinsic to the Debye equation when applied to A2, is that A2 can take all possible orientations and hence A1 will take all possible spatial orientations.

From this test it was also possible to infer what conditions may be needed to perform this experiment in a TEM. It was found that an objective aperture defining a scattering range of 0.16 Å$^{-1}$ was a good compromise between the conflicting needs of spatial and angular resolution. The pixel size corresponding to the spatial resolution determined by the choice of objective aperture was $2.69 \times 2.69$ Å. These conditions are readily achievable in a TEM and correspond to a microscope employing an objective aperture of $\simeq 30$ µm and operating at a magnification of 96000×, assuming an image pixel size of 26 µm.
5.6 Variance Measurements from Dark Field Images

Finally a comparison is made between the $V(Q)$ curves measured from model A2 and B2 using the simulated tilted dark field technique. The curves, shown in fig(5.16), exhibit many small fluctuations, however there is still sufficient difference between the two curves to suggest that the tilted dark field technique is sensitive to a higher order density correlation function and could be used to differentiate materials which are indistinguishable using more standard types of structural investigation.

In order to gauge the difference between the two $V(Q)$ curves a measure of their linear correlation coefficient [34], $r$, was made where

$$r = \frac{\sum_i(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i(x_i - \bar{x})^2 \sqrt{\sum_i(y_i - \bar{y})^2}}}.$$  

(5.26)

In eqn(5.26) $(x_i, y_i), i = 1, ..., N$, are coupled quantities and $\bar{x}$ and $\bar{y}$ are the means of the values $x_i$ and $y_i$.

$r$ is a measure of the degree of association between the variables $x$ and $y$ and can take any value in the range $-1 \leq r \leq 1$. When $r$ has a magnitude of 1, $x$ and $y$ lie along a straight line and are described as being completely correlated. This means that a knowledge of $x$ will allow the determination of $y$ and that a knowledge of $y$ will allow the determination of $x$. If however $r \approx 0$, $x$ and $y$ are considered to be uncorrelated and a knowledge of either of them will not allow the determination of the other.

The result of the test was $r_{V_{A2B2}}^2 = 0.68$. For comparative reasons a similar test was also performed on $G(r)$ curves measured from models A2 and B2. The result obtained was $r_{G_{A2B2}} = 0.96$.

Both $V(Q)$ and $G(r)$ are functions that are dependent on density correlation functions, $V(Q)$ on a pair-pair correlation function and $G(r)$ on a pair correlation.
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function. If the test was to give similar results for the correlation between the two sets of curves $V(Q)$ and $G(r)$, obtained from the different models, it could be concluded that even though there is an observed difference between the two $V(Q)$ curves it is no greater than that in the $G(r)$. However the difference between the values of $r$ obtained indicates that the tilted dark field technique is able to obtain extra structural information from the models.

![Graph](image)

**Figure 5.16:** The two $V(Q)$ curves exhibit many small fluctuations, however they still deviate from each other enough to suggest that $V(Q)$ can be used to investigate higher order correlation functions in amorphous materials.

### 5.7 Discussion

In a simulated environment dark field images of amorphous solids have been shown to contain structural information that cannot be obtained through a standard analysis of the diffraction pattern formed from the same material. This information is potentially very useful as a further means of discriminating between structural models, thus helping to alleviate the problem of uniqueness often encountered when performing structural investigations.
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The information is obtained by measurement of the normalised variance, $V(Q)$, of the intensity in the image though it could also be obtained through direct measurement of the mean of the square of the intensity, $I_{image}^2(Q)$. It seems from these investigations that it might also be possible to access other density correlation functions through measurement of other statistical properties of dark field images, such as the mean of the intensity cubed which is more commonly referred to as the third moment of a population distribution. In this case the population is derived from intensity within the dark field image.

The function $V(Q)$ itself is clearly sensitive to short range order, as has been shown theoretically through the simple calculations from the $n$ membered planar polygons. To make these measurements of short range order experimentally a reasonably high magnification must be used. This requires an increase in the size of the objective aperture which in turn decreases the angular resolution. The balance required between the angular and spatial resolution has already been discussed, but the result that these measurements can be made using a magnification of $\approx 96000 \times$ and a 30$\mu$m objective aperture suggests that the proposed tilted dark field method could be achieved in an experimental environment. There is however an apparent experimental difficulty which would arise from handling the low intensities found in dark field images formed with parallel illumination at the specified magnification.

Though similar to variable coherence microscopy, in terms of the analysis of dark field images, the proposed tilted dark field method does not seek to control coherence to examine microstructure. Instead parallel illumination is employed and angular resolution is used to control the size of a columnar volume which samples atomic configurations within the specimen. At an experimental level the difference between the two techniques is the type of illumination used. Variable coherence microscopy employs hollow cone as opposed to tilted dark field illumination. It is this fundamental difference in illumination that separates the two techniques.
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Having highlighted the fact that the tilted dark field method has detected some difference between the two models, it must be conceded that this difference is only small and has not yet been duplicated experimentally, whereas variable coherence microscopy has detected significant structural changes in amorphous germanium in an experimental environment. Thus, whilst the proposed tilted dark field technique is different to variable coherence microscopy, presently it is not as sensitive and a significant amount of work remains to be done before it can be considered to be a viable structural investigative technique.
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Conclusions and Suggestions for Further Work

In this Chapter the three diffraction based electron-optical techniques presented in Chapters 3, 4 and 5 are reviewed. The review emphasises the strengths and weaknesses of the different techniques as well as suggesting how the techniques can be further developed.

6.1 Plasmon Dispersion Analysis

Plasmon dispersion analysis (PDA) is performed using the same hardware that is employed to perform reduced density function (RDF) analysis. The only practical difference between PDA and RDF analysis being the region of the electron energy loss spectrum that is analysed. Though this practical difference is only small,
to effect PDA a number of more complicated changes have to be made to the software which controls the electron diffraction experiment. Also, the theory used to understand the experimental observations changes in emphasis from diffraction physics to solid state physics.

Currently, as has been mentioned, PDA is a semi-automated technique and work needs to be done in two areas to make PDA a fully automated technique.

- During data collection, a method for determining the signal to noise ratio in the plasmon peak must be developed, so that the experimentalist is not required to monitor and interrupt the experiment when the signal to noise ratio in the plasmon peak becomes too small. It seems feasible for software to be developed to perform this task. Alternatively, this problem could be avoided altogether through the use of a detector with a larger dynamic range than the photo-diode array that is currently being employed.

- The other area that needs automation is the analysis of the collected data. At present the plasmon peak positions are determined using a peak fitting routine that is applied manually to each individual momentum-resolved electron energy loss spectrum. Once again it seems feasible that software could be developed to automate this procedure.

Having performed these two tasks PDA would be a fully automated technique.

The interpretation of the plasmon dispersion measurements is somewhat limited by the fact that the theory of plasmon dispersion is based on the assumption that the material being investigated can be approximated by a solid in which the valence electrons form an electron gas moving in a uniform background of positive charge. Whilst this theory has been successfully applied to alkali metals, though some anomalies have been observed [1], and can be extended to include more complicated systems [2], there seems to be little more than a fundamental understanding of plasmon dispersion in materials that are not adequately de-
scribed by a free electron gas. Even though it is easy to recognise that there is a need for theoretical development in this area, it is also understood that this is not an easy task. In materials that are not well approximated by a free electron gas simplifying assumptions, such as the random phase approximation, can no longer be employed. This means that analytical solutions of the dielectric function for a material are no longer possible. Despite the difficulties, to extract the maximum amount of information from the measurements that can be made using PDA there needs to be a better theoretical understanding of plasmon dispersion in these materials.

Perhaps the greatest strength of this technique, in the current stage of its development, is that plasmon dispersion is particularly sensitive to the atomic and electronic structure within a material and as such materials which are structurally similar have quite distinctive plasmon dispersion relations. As well, PDA can be used in conjunction with EFDP to perform a range of sophisticated microanalytical measurements.

6.2 Reduced Density Function Analysis using Convergent Electron Illumination

In Chapter 4, a technique is proposed that utilises electron diffraction patterns formed using convergent electron illumination, to perform RDF analysis from smaller specimen volumes. As the electron diffraction patterns formed using convergent electron illumination do not satisfy the requirement that intensity at a point \( p \) in the diffraction pattern is derived from a unique scattering parameter \( Q \), the diffraction data must be deconvoluted before it is converted into an RDF.

The use of deconvolution techniques is provisional, based on the assumptions that the converged illumination is incoherent and that the diffraction patterns formed from each of the different illumination directions are identical. Whilst the assumption of incoherency is a reasonable approximation for all convergence
angles, the assumption that the diffraction patterns formed from the different illumination directions are identical is not. This is because as the convergence angle is increased, to illuminate smaller specimen volumes, a limit is reached after which micro-diffraction patterns are formed. Clearly micro-diffraction patterns do not satisfy the assumption that the diffraction pattern formed from each of the different illuminating directions is identical. This problem cannot be overcome, it must simply be avoided. Fortunately this can be done through visual inspection of the diffraction pattern.

As discussed previously, see Section 4.7, the main problem that must be solved to increase the accuracy of this technique and hence its range of application is the differentiation between forward elastically scattered electrons and unscattered electrons. The unscattered electrons contribute intensity to the converged electron diffraction pattern and this contribution becomes larger as the degree of convergence is increased. This intensity is unaccounted for in the deconvolution algorithm and as such will introduce error into the deconvolution estimate. To overcome this problem an estimate of the intensity contributed to the converged electron diffraction pattern, by unscattered electrons, needs to be made.

A large part of Chapter 4 is devoted to the comparison of deconvolution techniques and their suitability for application in different situations. While these techniques are used, in this thesis, for the specific purpose of extracting data from convergent beam diffraction patterns. In general, they are used to increase the resolution of experimental measurements and in particular digitally recorded images. As such, the continued development of these techniques is beneficial for electron diffraction studies in which more data is being recorded digitally.

Essentially the technique presented in Chapter 4 results from the combination of electronically recorded data and numerical methods. This combination is becoming more common, due to the development of sophisticated electronic recording devices, and its benefits are an increase in the amount of information that can
be extracted from experimental measurements.

6.3 Structural Analysis of Amorphous Materials using Dark Field Imaging

Using electron imaging in combination with electron diffraction is one way forward in addressing the problem of more completely determining the structure of amorphous materials. At present quantitative measurements of interatomic distances can only be obtained using RDF analysis, and even though this information is very useful, in many situations it is insufficient to solve materials problems. Electron imaging, which can provide two dimensional structural information is very useful for supplementing the data that can be obtained through RDF analysis.

One of the main problems with the technique proposed in Chapter 5 is that even though it can differentiate between the two similar amorphous models this difference is only small. A further problem is that the $V(Q)$ curves don't have distinctive peaks or troughs, instead the curves tend to fluctuate. Both of these problems could be due to the manner in which the larger models, used to perform the tilted dark field analysis, were prepared.

The preparation method involved rotating the smaller amorphous models, developed using Car-Parrinello molecular dynamics, at random and then utilising the different orientations of the smaller models to build the larger models. As mentioned earlier, see Section 5.4, this method for producing large models ($\approx 9000$) atoms avoids problems due to the large amounts of time required to develop these models using molecular dynamics. However it does have the potential to place atoms in unphysical positions at the interface between each building block.

To check the validity of the larger models, $G(r)$ curves were measured from the larger models and compared with those of the smaller models. The results showed
that, from the point of view of $G(r)$, the larger models are valid models of amorphous materials. However as the $G(r)$ reveals the average structure in the models and most of the atoms are in physically sensible positions, $G(r)$ may not be particularly sensitive to the unphysically positioned atoms. Alternatively the determination of $V(Q)$, using Cerius 2, does not involve any averaging of the structure in the model and is thus more sensitive to atoms in unphysical positions. The consequences of having atoms in unphysical positions distributed throughout the models are a reduction in the difference between the models, and irregularities in the structure of the models. These irregularities could account for the fluctuations observed in the $V(Q)$ curves. To resolve this problem a much simpler model must be constructed so that features in $V(Q)$ are unambiguously related to structure within the model.

The advantage of the proposed tilted dark field technique is that it can provide access to information that is dependent upon higher order correlation functions. This information cannot be readily acquired through more standard electron diffraction techniques and as such is useful in supplementing information that is already known about amorphous materials.
References Chapter 6
