Table of Contents

List of Figures ........................................................................................................... 7
List of Tables ............................................................................................................. 18
List of Abbreviations ................................................................................................. 20
Notation ..................................................................................................................... 21
Abstract .................................................................................................................... 24
Declaration ............................................................................................................... 25
Copyright Statement ................................................................................................. 26
Acknowledgements .................................................................................................. 27

Preface ......................................................................................................................... 28

1. INTRODUCTION AND OVERVIEW .................................................................. 31
   1.1 Nuclear Fission .................................................................................................. 31
      1.1.1 Competing Processes with Fission .............................................................. 33
   1.2 The Neutron Moderator .................................................................................... 37
      1.2.1 Requirements of a Neutron Moderator ...................................................... 37
      1.2.2 Moderating Materials ................................................................................. 39
      1.2.3 Graphite as a Moderating Material ............................................................ 40
   1.3 Structure and Material Properties of Graphite ............................................... 40
   1.4 Preparation of Nuclear Grade Graphite ........................................................... 43
   1.5 Grades of Graphite ........................................................................................... 46
      1.5.1 Pile Grade A ............................................................................................... 46
      1.5.2 Gilsocarbon ............................................................................................... 47
      1.5.3 Comparison of the Material Properties of PGA and Gilsocarbon .......... 49
   1.6 Graphite-Moderated Reactors in the United Kingdom ..................................... 51
      1.6.1 Early Graphite-Moderated Reactors ............................................................ 53
      1.6.2 The Magnox Reactor ................................................................................... 54
      1.6.3 The Advanced Gas-Cooled Reactor ............................................................. 56
      1.6.4 Next-Generation Graphite Moderated Reactors ....................................... 58
1.7 Conclusions and Research Objectives .......................................................... 60

2. LITERATURE REVIEW .................................................................................... 62
   2.1 Studies into the Fundamental Material Properties of Graphite ................. 63
      2.1.1 Young’s Modulus and Deformation in Graphite ............................... 63
      2.1.2 Porosity in Graphite ....................................................................... 68
      2.1.3 Radiation-Induced Defects in Graphite ......................................... 70
      2.1.4 Stress in Reactor Components ....................................................... 71
   2.2 Studies into the Effects of Stress on Nuclear Grade Graphite .................. 74
      2.2.1 Studies by the Japanese Atomic Energy Research Institute ............ 75
      2.2.2 Studies by the University of Manchester ........................................ 81
         2.2.2.1 Study by Bakenne (2012) ....................................................... 81
         2.2.2.2 Study by Bodel (2012) ......................................................... 84
      2.2.3 Other Studies into the Effects of Stress on the Properties of Graphite ... 92
      2.2.4 Studies into the Pore Structure of Graphite .................................... 96
   2.3 Studies into the Relationship between Porosity and Young’s Modulus ....... 97
   2.4 Conclusions and the Proposed Experimental Program .......................... 101
      2.4.1 Conclusions ................................................................................. 101
      2.4.2 Experimental Proposal .................................................................. 103
   2.5 Summary ................................................................................................. 105

3. PRELIMINARY MATERIALS ACQUISITION AND CHARACTERISATION ........... 107
   3.1 Preliminary Materials Acquisition and Characterisation .......................... 107
   3.2 Sample Preparation ............................................................................... 108
      3.2.1 Preparation of Confocal Laser Microscopy Samples ...................... 108
      3.2.2 Preparation of X-ray Tomography Samples .................................. 111
      3.2.3 Preparation of X-ray Crystallography Samples ............................. 112
   3.3 Sample Metrology .................................................................................. 113
   3.4 Summary ................................................................................................. 116

4. CONFOCAL LASER MICROSCOPY EXPERIMENTS ........................................ 118
   4.1 Introduction to Confocal Laser Microscopy .......................................... 118
4.1.1 Theory of Microscopy ................................................................. 118
4.1.2 Theory of Confocal Laser Microscopy ........................................ 120
4.2 Materials and Apparatus .................................................................. 122
  4.2.1 The Confocal Microscope ......................................................... 122
  4.2.2 The Axial Compression Rig ....................................................... 124
  4.2.3 Samples and Sample Preparation ............................................... 126
4.3 Preliminary Investigations into Stress-Strain and Deformation Properties of Graphite ................................................................. 126
  4.3.1 Investigation 1: PGA Compressed Perpendicular to the Grain Direction 128
  4.3.2 Investigation 2: PGA Compressed Parallel to the Grain Direction ...... 132
  4.3.3 Investigation 3: Gilsocarbon ..................................................... 133
  4.3.4 Conclusions ............................................................................ 135
4.4 Imaging during Loading and Unloading ............................................. 135
4.5 In-Situ Confocal Laser Microscopy Images ........................................ 137
4.6 Analyzing the Suitability of Sample Geometries .................................. 144
4.7 Image Segmentation and Segmentation Errors ................................... 147
4.8 Pore Dimensional and Property Analysis .......................................... 153
  4.8.1 Pore Areas ............................................................................ 154
  4.8.2 Pore Eccentricity ................................................................. 160
  4.8.3 Pore Orientation ................................................................. 168
  4.8.4 Pore Angularity .................................................................... 176
    4.8.4.1 Calculation of Pore Angularity ............................................ 177
  4.8.5 Pore Separation Analysis......................................................... 183
    4.8.5.1 Nearest Neighbour Analysis .............................................. 185
    4.8.5.2 Voronoi Analysis ........................................................... 188
4.9 Conclusions ................................................................................... 191
4.10 Summary ...................................................................................... 195

5. X-RAY COMPUTED TOMOGRAPHY EXPERIMENTS .............................. 197
5.1 Introduction to X-Ray Computed Tomography .................................. 197
  5.1.1 Theory of X-ray Tomography ................................................ 197
5.2 Materials and Apparatus .................................................................. 200
5.2.1 The Tomography Scanner ................................................................. 200
5.2.2 The Axial Compression Rig ............................................................ 201
5.2.3 Samples and Sample Preparation .................................................... 202
5.3 Imaging during Loading ..................................................................... 203
5.4 Data Reconstruction, Image Segmentation and Segmentation Errors .... 204
5.5 In-Situ X-ray Tomography Images ...................................................... 207
5.6 Pore Dimensional and Property Analysis ............................................. 211
  5.6.1 Pore Volumes ................................................................................. 202
    5.6.1.1 Comparison to Confocal Laser Microscopy Data ..................... 219
  5.6.2 Pore Eccentricity ........................................................................ 224
    5.6.2.1 Comparison to Confocal Laser Microscopy Data ................. 234
  5.6.3 Pore Surface Areas ....................................................................... 237
    5.6.3.1 Comparison to Pore Volume Data ........................................ 241
  5.6.4 Pore Angularity ........................................................................... 245
    5.6.4.1 Comparison to Confocal Laser Microscopy Data ................ 247
5.7 Conclusions ....................................................................................... 250
5.8 Summary .......................................................................................... 252

6. X-RAY CRYSTALLOGRAPHY EXPERIMENTS ........................................... 255

  6.1 Introduction to X-Ray Crystallography ................................................ 255
    6.1.1 Theory of X-ray Diffraction ....................................................... 256
  6.2 Materials and Apparatus .................................................................... 257
    6.2.1 The X-Ray Diffraction Scanner .................................................. 257
    6.2.2 The Axial Compression Rig ....................................................... 258
    6.2.3 Samples and Sample Preparation .............................................. 258
  6.3 X-Ray Diffraction ............................................................................. 260
  6.4 Diffraction Spectra Analysis .............................................................. 261
    6.4.1 Miller Indices ............................................................................ 266
    6.4.2 Unit Cell and Layer Spacing Parameters ................................... 270
      6.4.2.1 Unit Cell Parameters ......................................................... 275
    6.4.3 Lattice Strain and Crystallite Size .............................................. 278
      6.4.3.1 Crystallite Size ................................................................ 285
The number of words in the main text of this thesis is 71316.
List of Figures

Figure 1.1: Graph showing the mechanisms of interaction between charged particles and the ranges at which the interactions operate. $B_c$ represents the Coulomb barrier. .................................................................32

Figure 1.2: The relationship between cross-section and energy following neutron absorption by a uranium-235 nucleus. The processes shown are fission (n,f), elastic scatter (n,n), inelastic scatter (n,n’) and radiative capture (n,γ) [2]. .................................35

Figure 1.3: The relationship between cross-section and energy following neutron absorption by a uranium-238 nucleus. The processes shown are fission (n,f), elastic scatter (n,n), inelastic scatter (n,n’) and radiative capture (n,γ) [2]. .........................36

Figure 1.4: The hexagonal lattice structure of graphite [9]. .................................................42

Figure 1.5: The unit cell of the hexagonal lattice is shown in bold [8]. ..............................42

Figure 1.6: The stages of manufacturing graphite from petroleum coke suitable for use in fission reactors. Image adapted from Nightingale [10]. .................................................44

Figure 1.7: Microscopy image showing the microstructure of PGA graphite. A few filler particles are highlighted. The preferential alignment of the filler particles from the top to the bottom of the image, i.e. along the extrusion direction, is visible. .......47

Figure 1.8: Microscopy image showing the microstructure of Gilsocarbon. Spherical filler particles are clearly visible, as well as significant porosity. ..........................48

Figure 1.9: Schematic of a Magnox reactor. .................................................................48

Figure 1.10: Cutaway of an AGR fuel assembly. Each assembly contains a circular array of 36 fuel rods, each of which contains 20 enriched uranium oxide pellets. Each assembly is surrounded by a graphite sleeve [19]. .....................................57

Figure 1.11: Schematic of an advanced gas-cooled reactor [20]. ..................................58

Figure 2.1: Stress-strain behaviour for a PGA graphite sample. Three loading-unloading cycles are shown, and permanent deformation can be observed. ..........64

Figure 2.2: Theoretical and experimentally derived stress strain relationship for PGA graphite [21]. ..........................................................................................................................66

Figure 2.3: The formation of a displacement cascade induced by collisions of neutrons with the carbon lattice. Image courtesy of G. Hall.................................70

Figure 2.4: Interstitial and vacancy loops in the graphite lattice. Image adapted from Thrower [33]. ..................................................................................................................71
Figure 2.5: Image showing an Oldbury Magnox fuel rod being inserted into the channel running through the centre of a keyed graphite brick. Image courtesy of B. Marsden, University of Manchester. .................................................................72

Figure 2.6: Composite image showing a large scale fracture path of a graphite component from a British AGR reactor. Image courtesy of G. B. Heys, UK Nuclear Installations Inspectorate [35]. .................................................................73

Figure 2.7: Variation of Young’s modulus with compressive strain (left) and tensile strain (right). Hysteresis loops from repeated loading and unloading are visible in both cases [36]. .................................................................................76

Figure 2.8: Left: Change in Young’s modulus for a number of nuclear graphites with increasing compressive pre-stress [37]. Right: Theoretical expressions from Walsh [43] fitted to the experimental data [37].................................................................................77

Figure 2.9: Young’s modulus against total porosity for Gilsocarbon and PGA. No load has been applied. Measurements for PGA with the grain direction (WG) and against to the grain direction (AG) are shown [45].................................................................82

Figure 2.10: DYM and shear modulus in PGA graphite plotted against open pore volume (OPV) before and after loading. Top: Measurements with the grain. Bottom: Measurements against the grain [45].................................................................................83

Figure 2.11: Dynamic Young’s modulus plotted against density for four grades of graphite, including data with and against the grain for anisotropic PGA (PGA WG and PGA AG respectively), determined using time of flight methods [46]. ..........85

Figure 2.12: Young’s modulus plotted against density for isotropic graphites, determined using the impact excitation technique [46] ........................................87

Figure 2.13: Schematic of the four point bend testing rig. There are four points of contact with the sample (hence the name) and the two uppermost spans push the centre of the sample downwards until failure occurs. ........................................88

Figure 2.14: Variation in transmission velocity with applied load. The sample is PGA compressed perpendicular to the grain, and the longitudinal pulse is being measured. Repeated loading and unloading were performed on the sample [46] . 89

Figure 2.15: Micrographs of the surface of graphite as a PGA sample is axially loaded, produced using a confocal laser scanning microscope. Image adapted from Bodel [46]. Significant deformation is observed in the elliptical filler particle near the centre of the image. .........................................................................................91

Figure 2.16: Stress distribution in a block of H-451 graphite at the end of its operational lifetime. Points A and B are defined for further study. Unit: Pa [55].....93

Figure 2.17: Variation of internal stress build-up with time in an H-451 graphite component measured at the two locations defined in Figure 2.16 [55].................93
Figure 2.18: Change in Young’s modulus with fast neutron dose. $E_0$ represents the unirradiated Young’s modulus, while $E_{x,y,z}$ represent moduli measured in the $x$-, $y$- and $z$-directions respectively [48].

Figure 2.19: Probability distribution function of pore shapes defined by ellipses. The second derivative of the intensity function in the range $0.95 < e < 1$ is inset [56].

Figure 2.20: Effect of porosity on elastic properties of graphite [50].

Figure 2.21: Image showing the possible transducer orientations with respect to the grain of anisotropic graphite. Image courtesy of W. Bodel [46].

Figure 3.1: The Gilsocarbon block used as the source material for Gilsocarbon samples during this project. Block dimensions are 23.3 cm long and 10.4 cm wide.

Figure 3.2: The Pile Grade A graphite block used as the source material for PGA samples during this project. The extrusion direction is vertical through the sample. Block dimensions are 20.8 cm long and 20.6 cm wide.

Figure 3.3: Confocal microscope images of an unpolished region (left) and a polished region (right) of a Gilsocarbon sample. Both images are of the same resolution and size. Polishing produces a significantly smoother and more reflective surface, allowing the microstructure to be observed in greater detail.

Figure 3.4: Typical samples used during the confocal microscopy experiments. Left: a Gilsocarbon sample that sheared horizontally into two pieces. Middle: An unloaded Gilsocarbon sample that is fully intact. Right: A PGA sample that has sheared diagonally.

Figure 3.5: A typical Gilsocarbon sample used during the X-ray tomography experiments. Samples were machined to have a cross-sectional area of 8 mm and height 10 mm.

Figure 3.6: Typical samples used during the X-ray diffraction experiments. Samples were machined to have a cross-sectional area of 7 mm and height 2-4 mm.

Figure 3.7: The three typical sample geometries used during this project. Left: A thin cylindrical Gilsocarbon sample used for X-ray diffraction. Middle: A Gilsocarbon sample machined into a cuboid used for confocal laser microscopy. Right: A cylindrical Gilsocarbon sample used for X-ray tomography.

Figure 4.1: Schematic of a simple microscope showing magnification of an object using two lenses. The red dots represent the focal lengths of each lens. The observer sees a highly magnified virtual image.

Figure 4.2: Schematic showing a confocal laser scanning microscope. Only beams that reach the detector are shown; other beams will be present but are blocked by the apertures.
Figure 4.3: The Olympus OLS 4000 confocal laser microscope. Multiple lenses allow images of a range of magnifications to be produced. The mobile sample stage allows different regions of the sample to be scanned and stitched together with high precision. The sample stage can be controlled automatically by the microscope software, or manually using the controller at the bottom-right of the image.

Figure 4.4: Two separate images of a PGA sample stitched together by the confocal microscope software. Image distortion can be seen vertically within the red highlighted area, which represents the overlap region where stitching has taken place.

Figure 4.5: The Deben MICROTEST 5 module compressing a Gilsocarbon sample.

Figure 4.6: The loading rig mounted on the sample stage of the confocal laser microscope. This experimental arrangement was used to acquire images of the samples while the applied load was held steady.

Figure 4.7: Plot of the applied force against contraction for a PGA sample compressed perpendicular to the grain direction. The first loading-unloading cycle is shown in blue, followed by subsequent cycles coloured red and green. The regular notches in each of the loading cycles indicate when loading was paused for confocal laser microscopy image acquisition.

Figure 4.8: Plot of stress against strain for a PGA sample compressed perpendicular to the grain direction.

Figure 4.9: Plot of applied force against contraction for a PGA sample compressed parallel to the grain direction. The first loading-unloading cycle is shown in blue, followed by subsequent cycles coloured red and green.

Figure 4.10: Plot of applied force against contraction for a sample of Gilsocarbon. Four separate loading-unloading cycles are observed, and unexpected failure of the sample was observed during the second cycle, coloured red.

Figure 4.11: Four images of a region of a Gilsocarbon sample, recorded at zero load. Clockwise from top left: Colour image of the sample, greyscale image of the sample, three-dimensional heightmap of the sample, two-dimensional heightmap of the sample. The scale for all images, shown at the bottom left, is the same.

Figure 4.12: Images of Gilsocarbon taken at a range of applied loads. The compressive load was applied horizontally in the images. The final image shows sample failure.

Figure 4.13: Four images of PGA-AG taken at a range of applied loads. The compressive load was applied horizontally in the images.

Figure 4.14: Four images of PGA-WG taken at a range of applied loads. The compressive load was applied horizontally in the images.
Figure 4.15: Variation of mean pore areas for a range of differently sized regions of interest. A quadratic curve is fitted to the data. Five regions of interest were selected for each region size except for the largest size, which corresponded to the entire sample surface, hence was only measured once.

Figure 4.16: Brightness curves for the Gilsocarbon (left) and PGA (right) samples.

Figure 4.17: (i) Two dimensional micrograph of a full Gilsocarbon graphite sample. (ii) A higher resolution section of the image in (i). (iii) Thresholded and binarised representation of image (ii). Open pores are coloured black, while all other features are white. Notations on the image show regions of binder phase (B), filler particles (F) and open pores (P). (iv) A small subsection of the same sample viewed in 3D.

Figure 4.18: Graph showing variation of mean pore area at different thresholding levels for Gilsocarbon graphite. The lower and upper bounds for reasonable thresholding were 37 and 43 respectively, resulting in a thresholding limit of 40 and errors of +7.94% and -6.69%. These errors are shown on the graph for each mean pore area value.

Figure 4.19: Graph showing variation of mean pore area at different thresholding levels for PGA graphite. The lower and upper bounds for reasonable thresholding were 34 and 40 respectively, resulting in a thresholding limit of 37 and errors of +7.27% and -5.65%. These errors are shown on the graph for each mean pore area value.

Figure 4.20: Graph showing pore area distributions for a Gilsocarbon sample with zero load applied. Data are grouped into bin size of 10 µm². No data is available for pores below 50µm². In each case a tail extends to the right, beyond the region shown above. The visible range in each graph corresponds to over 99% of the data points.

Figure 4.21: Graph showing pore area distributions for a PGA sample with zero load applied. Data are grouped into bin size of 10 µm². No data is available for pores below 50µm². In each case a tail extends to the right, beyond the region shown above. The visible range in each graph corresponds to over 99% of the data points.

Figure 4.22: Pore area distributions for Gilsocarbon and PGA graphite, plotted on logarithmic axes. A power law has been fitted to each data series.

Figure 4.23: Graph showing variation of pore areas at the surface of PGA and Gilsocarbon samples during the application of an axial load.

Figure 4.24: The range of pore eccentricities observed in Gilsocarbon and PGA samples with zero applied load. An eccentricity of zero represents a perfect sphere,
while progressively larger values indicate the pore has an increasingly large aspect ratio. Pores defined by poorly-fitting ellipses have been removed. ..........................163

Figure 4.25: Scatter graph showing the area and eccentricity of each pore (well defined by an ellipse) in the Gilsocarbon sample. ......................................................164

Figure 4.26: Variation of mean pore eccentricity for PGA and Gilsocarbon graphite during the application of axial compressive loads ..............................................................165

Figure 4.27: Schematic showing example behaviour of different orientations of highly eccentric pore, and the effects of axial loading upon their eccentricity. Arrows indicate the loading direction. .................................................................166

Figure 4.28: Loading-induced variation of mean pore eccentricity in PGA-WG. Three sets of data are shown – all pores, pores oriented within ±10° of the loading axis (parallel oriented) and pores oriented 80-100° from the loading axis (perpendicular oriented) ..................................................................................................................168

Figure 4.29: Schematic showing the definition of pore orientation angle measured anticlockwise from the loading axis .................................................................................169

Figure 4.30: Pore orientation distribution in the Gilsocarbon sample at a range of applied loads. ................................................................................................................170

Figure 4.31: Pore orientation distribution in the PGA-AG sample at a range of applied loads, with a best fitting third order polynomial curve applied. .........................171

Figure 4.32: Pore orientation histograms for PGA and Gilsocarbon samples at zero load. The PGA-AG data has a third order polynomial curve fitted to it. ..................172

Figure 4.33: Pore orientation histograms for the PGA-WG sample at zero load. The data has a second order polynomial curve fitted to it ...........................................174

Figure 4.34: Graph showing percentage change of mean pore orientation angle with increasing load. Pore orientation at zero load is defined as 0%, and any subsequent pore rotation is expressed as a percentage from this value. Angles are defined from the loading axis, rotating anti-clockwise. Best-fitting lines are fixed to travel through the origin ........................................................................................................175

Figure 4.35: Definitions of form, angularity and texture for a particle. Image adapted from Little et al. [68]. ............................................................................................177

Figure 4.36: Rate of change of the measure of angularity with increasing stress for Gilsocarbon and PGA samples .................................................................................181

Figure 4.37: Images showing a segmented and binarised region of a Gilsocarbon sample (left) and the Voronoi diagram for this region (right) ........................................185

Figure 4.38: Variation of mean nearest neighbour pore distances during the application of loads in Gilsocarbon .................................................................................186
Figure 4.39: Variation of mean nearest neighbour pore distances during the application of loads in PGA. ................................................................. 186

Figure 4.40: Variation of mean Voronoi cell size for a Gilsocarbon sample during the application of an axial compressive load. ........................................ 188

Figure 4.41: Variation of mean Voronoi cell size for a PGA sample during the application of an axial compressive load. ........................................ 189

Figure 4.42: Variation of mean Voronoi cell size for a Gilsocarbon sample with pore regions subtracted out. ......................................................... 190

Figure 4.43: Variation of mean Voronoi cell size for PGA samples with pore regions subtracted out. ................................................................. 190

Figure 4.44: Image showing the stress distribution within a sample compressed along the vertical plane. Contours represent relative intensity of stresses, and the shaded regions are the most severely stressed [71]. ........................................ 194

Figure 5.1 : A simplified schematic of an X-ray tomography scanner. ............ 198

Figure 5.2: Internal view of the Nikon Metrology 320/225 kV Custom Bay. The X-ray source, detector and sample stage are labelled on the image....................... 201

Figure 5.3: The loading rig used in the X-ray tomography experiments and the laptop used to control the rig. ............................................................... 202

Figure 5.4: Thresholding curves for the Gilsocarbon (left) and PGA (right) samples. ........................................................................................................ 206

Figure 5.5: Graph showing variation of mean pore area at different thresholding levels for Gilsocarbon graphite. The lower and upper bounds for reasonable thresholding were 22 and 28 respectively, resulting in a thresholding limit of 25 and errors of +6.52% and -11.11%. These errors are shown on the graph for each mean pore area value. ........................................................................ 206

Figure 5.6: Graph showing variation of mean pore area at different thresholding levels for PGA graphite. The lower and upper bounds for reasonable thresholding were 13 and 17 respectively, resulting in a thresholding limit of 15 and errors of +5.80% and -4.69%. These errors are shown on the graph for each mean pore area value. ........................................................................ 207

Figure 5.7: Three-dimensional representation of a Gilsocarbon sample acquired using X-ray tomography. ............................................................ 208

Figure 5.8: Three-dimensional representations of PGA samples acquired using X-ray tomography. Left: Grain direction is horizontal in the image. Right: Grain direction is vertical in the image......................................................... 209
Figure 5.9: A single two-dimensional slice through the centre of an unloaded Gilsocarbon sample. Contrast has been enhanced to aid clarity. ........................................210

Figure 5.10: A single two-dimensional slice through the centre of an unloaded PGA sample. Contrast has been enhanced to aid clarity..................................................210

Figure 5.11: Distribution of the range of pore volumes present in the Gilsocarbon sample with a token external load applied. A logarithmic y-axis is used to increase readability of data. The observed relationship is well described by a power law. .214

Figure 5.12: Distribution of the range of pore volumes present in the PGA samples with a token external load applied. A logarithmic y-axis is used to increase readability of data. The observed relationships are well described by power laws. .................................................................................................................................214

Figure 5.13: Pore volume distributions for Gilsocarbon and PGA graphite samples, plotted on logarithmic axes. A power law has been fitted to each data series. .....215

Figure 5.14: Mean pore volumes at a range of applied loads for each graphite sample. Stresses are shown as a ratio to the expected failure load of the sample calculated using Equation 4.2 and data from Table 5.2. Quadratic best-fitting curves are shown for each sample........................................................................................................................................216

Figure 5.15: Graph showing the residuals for the quadratic best-fitting curves in Figure 5.14.........................................................................................................................218

Figure 5.16: Comparison of observed variation in mean pore areas and volumes for data collected using X-ray tomography and confocal microscopy. .........................220

Figure 5.17: Variation in mean pore areas for five slices through the Gilsocarbon sample. ...................................................................................................................................222

Figure 5.18: Two distinct types of ellipsoid. Left: An oblate ellipsoid. Right: A prolate ellipsoid [77].............................................................................................................225

Figure 5.19: The range of pore eccentricities observed in Gilsocarbon and PGA samples with zero applied load. An eccentricity of zero represents a perfect sphere, while progressively larger values indicate the pore has an increasingly large aspect ratio....................................................................................................................228

Figure 5.20: Graph showing the change in mean pore eccentricity of each sample at a range of loads. The applied load is shown as a ratio to the expected failure load calculated using Equation 4.2 and the data in Table 5.2 ........................................229

Figure 5.21: Variation of pore eccentricity in Gilsocarbon, with pores split into five groups based upon their volumes. Each group contains twenty percent of the total number of pores..........................................................................................................................231
Figure 5.22: Variation of pore eccentricity in PGA-AG, with pores split into five groups based upon their volumes. Each group contains twenty percent of the total number of pores.

Figure 5.23: Variation of pore eccentricity in PGA-WG, with pores split into five groups based upon their volumes. Each group contains twenty percent of the total number of pores.

Figure 5.24: Range of eccentricities of pores at zero load, calculated using confocal microscopy and tomography.

Figure 5.25: Graph showing the stress induced variation of mean pore eccentricities in Gilsocarbon and PGA graphite, calculated using confocal laser microscopy and X-ray tomography data.

Figure 5.26: Variation of mean pore surface areas of PGA and Gilsocarbon samples during the application of a range of axial compressive loads. The applied loads are calculated as a ratio to the failure load calculated Equation 4.2.

Figure 5.27: The relationship between mean pore volumes and surface areas at varying levels of applied load for three graphite samples. Arrows indicate the direction of sample shrinkage as the applied load increased.

Figure 5.28: Relationship between mean pore volume and mean pore surface area for Gilsocarbon and PGA samples, with lines showing the volume-surface area relationship for a sphere, a cube and a tetrahedron.

Figure 5.29: A subsection of Figure 5.28 focussing on the region containing the experimental data on pore sizes.

Figure 5.30: Rate of change of the measure of angularity with increasing stress for Gilsocarbon and PGA samples.

Figure 6.1: Schematic of an X-ray diffraction apparatus.

Figure 6.2: Diffraction pattern for the Gilsocarbon sample.

Figure 6.3: Diffraction pattern for the PGA-AG sample.

Figure 6.4: Diffraction pattern for the PGA-WG sample.

Figure 6.5: Diffraction pattern for the Gilsocarbon sample, with the y-axis normalised.

Figure 6.6: Diffraction pattern for the PGA-AG sample, with the y-axis normalised.
Figure 6.7: Diffraction pattern for the PGA-WG sample, with the y-axis normalised.
..................................................................................................................265
Figure 6.8: Miller Indices of certain planes in a cubic cell. Image courtesy of Felix
King [82]. ........................................................................................................267
Figure 6.9: Miller indices for a hexagonal crystal. The three highlighted planes are
crystallographically equivalent to one other. ....................................................267
Figure 6.10: Miller-Bravais indices for a hexagonal crystal. The three highlighted
planes are crystallographically equivalent to one other. ......................................268
Figure 6.11: Diffraction pattern for graphite taken from the PDF-4 database
maintained by the International Centre for Diffraction Data (ICDD). ..................269
Figure 6.12: The derivation of Bragg’s Law between two layers of a crystal lattice.
For constructive interference of two X-rays to occur, the path length difference, 2d
sin\(\theta\), must be an integer number of wavelengths. ........................................270
Figure 6.13: Graph showing the angle of a peak plotted against the \(d_{002}\) spacing. 272
Figure 6.14: Graph showing the relationship between applied stress and \(c\)-spacing
for the Gilsocarbon, PGA-AG and PGA-WG samples. .........................................276
Figure 6.15: Graph showing the relationship between applied stress and \(a\)-spacing
for the Gilsocarbon, PGA-AG and PGA-WG samples. .........................................277
Figure 6.16: Williamson-Hall plot showing the derivation of the size and strain
components of a crystal lattice using data from a diffraction pattern. Image
courtesy of Barnes et al. [87]. .............................................................................280
Figure 6.17: Williamson-Hall plot for the PGA-AG samples at a range of different
loads. Best-fitting lines are not shown to ensure the data points themselves are
clear, and are quantified in Figure 6.20 instead. ................................................281
Figure 6.18: Williamson-Hall plot for the PGA-WG samples at a range of different
loads. Best-fitting lines are not shown to ensure the data points themselves are
clear, and are quantified in Figure 6.20 instead. ................................................282
Figure 6.19: Williamson-Hall plot for the Gilsocarbon samples at a range of different
loads. Best-fitting lines are not shown to ensure the data points themselves are
clear, and are quantified in Figure 6.20 instead. ................................................283
Figure 6.20: Graph showing the gradient of each best-fitting line plotted against the
applied load for each sample. The value of each point is proportional to the mean
inhomogeneous strain. .......................................................................................284
Figure 6.21: Y-intercept values of the best fitting lines of Figure 6.17, Figure 6.18
and Figure 6.19.....................................................................................................286
Figure 6.22: Values of crystallite size for each sample at a range of applied loads. 287
Figure 6.23: Variation of the Bacon Anisotropy Factor in Gilsocarbon and PGA graphite at a range of applied loads.
**List of Tables**

Table 1.1: The four competing processes that may occur upon absorption of a neutron by a uranium-235 nucleus.................................................................35

Table 1.2: Comparison of existing nuclear moderating materials with the advantages and disadvantages of each. ..............................................................................39

Table 1.3: The main types of graphite moderated nuclear reactor used for power generation, countries in which they are most commonly used and their dates of operation........................................................................................................40

Table 1.4: Some of the important material properties of PGA and Gilsocarbon. The anisotropy of PGA graphite results in different properties parallel and perpendicular to the extrusion/grain direction. These values are defined as WG (with grain) and AG (against grain). Data adapted from Brocklehurst and Kelly [17]..........................50

Table 1.5: A list of nuclear reactors that are, or have been, operational in the UK. Reactors with a shaded background are still operational at the time of writing, and the closure dates are current best estimates. ........................................................................52

Table 2.1: Comparison between static ($E_s$) and dynamic ($E_D$) Young’s moduli for six samples using the three experimental methods discussed above [46]. ..............................88

Table 2.2: An excerpt of Bodel’s quantitative results, showing Young’s moduli data derived from time of flight, compressive testing (denoted by $c$) and four point bend testing (denoted by $f$). WG and AG refer to measurements made with and against the grain respectively [46]. ..........................................................................................90

Table 3.1: Table showing details of the size and dimensional morphology of each Gilsocarbon sample, and information regarding the use of each sample..............114

Table 3.2: Table showing details of the size, dimensional morphology and usage of each PGA sample oriented with the loading axis parallel to the grain direction, and information regarding the use of each sample.............................................115

Table 3.3: Table showing details of the size, dimensional morphology and usage of each PGA sample oriented with the loading axis perpendicular to the grain direction, and information regarding the use of each sample..............................116

Table 4.1: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46]. .................................................................128

Table 4.2: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46]. Note that the cross-sectional area data provided is along the loading axis, and does not represent the surface being scanned by the confocal laser microscope. ..............................................136
Table 4.3: Mean pore eccentricity values before and after the ellipse fitting criterion was applied. Mean eccentricity increased upon application of the fitting criterion.

Table 5.1: Operational properties of the Nikon Metrology 320/225 kV Custom Bay.

Table 5.2: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46].

Table 5.3: A comparison of linear and quadratic fits for each graphite sample, with goodness of fit quantifies using linear regression analysis.

Table 5.4: The rate of change of pore areas and pore volumes due to growth of stresses, and the ratio between these variables.

Table 5.5: The rate of change of the mean measure of angularity due to growth of stresses, and the ratio between these variables.

Table 6.1: Operational parameters of the Philips Automatic Diffractometer used in the XRD experiments.

Table 6.2: Details of the samples upon which X-ray diffraction analysis was performed.

Table 6.3: The scanning parameters used for the XRD analysis of PGA and Gilsocarbon samples.

Table 6.4: Miller and Miller-Bravais indices and d-spacings for the peaks in the Gilsocarbon and PGA samples.

Table 6.5: Values of $a$, $c$, $d_{002}$ and unit cell volume for Gilsocarbon, PGA-AG and PGA-WG samples at zero load.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG</td>
<td>Against Grain</td>
</tr>
<tr>
<td>AGR</td>
<td>Advanced Gas-Cooled Reactor</td>
</tr>
<tr>
<td>BAEL</td>
<td>British Acheson Electrodes Limited</td>
</tr>
<tr>
<td>BAF</td>
<td>Bacon Anisotropy Factor</td>
</tr>
<tr>
<td>BEPO</td>
<td>British Experimental Pile-0</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
</tr>
<tr>
<td>CANDU</td>
<td>Canadian Deuterium-Uranium Reactor</td>
</tr>
<tr>
<td>CLM</td>
<td>Confocal Laser Microscopy</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>GLEEP</td>
<td>Graphite Low Energy Experimental Pile</td>
</tr>
<tr>
<td>HTR</td>
<td>High Temperature Reactor</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>JAERI</td>
<td>Japanese Atomic Energy Research Institute</td>
</tr>
<tr>
<td>Magnox</td>
<td>Magnesium-Oxygen Reactor</td>
</tr>
<tr>
<td>MSR</td>
<td>Molten Salt Reactor</td>
</tr>
<tr>
<td>MTR</td>
<td>Materials Test Reactor</td>
</tr>
<tr>
<td>PBR</td>
<td>Pebble Bed Reactor</td>
</tr>
<tr>
<td>PGA</td>
<td>Pile Grade A</td>
</tr>
<tr>
<td>PMR</td>
<td>Prismatic Block Reactor</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurized Water Reactor</td>
</tr>
<tr>
<td>RBMK</td>
<td>Reaktor Bolshoy Moshchnosti Kanalnyy (Russian)</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>UNGG</td>
<td>Uranium Naturel Graphite Gaz (French)</td>
</tr>
<tr>
<td>VHTR</td>
<td>Very High Temperature Reactor</td>
</tr>
<tr>
<td>VVER</td>
<td>Vodo-Vodyanoi Energetichesky Reaktor (Russian)</td>
</tr>
<tr>
<td>WG</td>
<td>With Grain</td>
</tr>
<tr>
<td>XCT</td>
<td>X-ray Computed Tomography</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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</table>
# Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>distance across a hexagonal unit cell</td>
</tr>
<tr>
<td>$A$</td>
<td>cross-sectional area</td>
</tr>
<tr>
<td>$A'$</td>
<td>elastic compliance</td>
</tr>
<tr>
<td>$A_n$</td>
<td>measure of angularity</td>
</tr>
<tr>
<td>$B_c$</td>
<td>Coulomb barrier</td>
</tr>
<tr>
<td>$c$</td>
<td>speed of light in a vacuum</td>
</tr>
<tr>
<td>$c$</td>
<td>nearest neighbour distance in hexagonal lattice</td>
</tr>
<tr>
<td>$d$</td>
<td>crystal layer spacing</td>
</tr>
<tr>
<td>$d$</td>
<td>resolution limit</td>
</tr>
<tr>
<td>$E$</td>
<td>energy</td>
</tr>
<tr>
<td>$E$</td>
<td>dynamic Young’s modulus</td>
</tr>
<tr>
<td>$E'$</td>
<td>moderating efficiency</td>
</tr>
<tr>
<td>$e$</td>
<td>eccentricity</td>
</tr>
<tr>
<td>$F$</td>
<td>force</td>
</tr>
<tr>
<td>$f$</td>
<td>thermal utilisation factor</td>
</tr>
<tr>
<td>$f'$</td>
<td>parameter dependent on pore geometry</td>
</tr>
<tr>
<td>$f_f$</td>
<td>fundamental flexural frequency</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational constant</td>
</tr>
<tr>
<td>$H$</td>
<td>height</td>
</tr>
<tr>
<td>$K$</td>
<td>shape factor</td>
</tr>
<tr>
<td>$k$</td>
<td>neutron reproduction factor</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$k_1$</td>
<td>correction accommodating Poisson’s ratio and beam dimensions</td>
</tr>
<tr>
<td>$L$</td>
<td>length</td>
</tr>
<tr>
<td>$L_a$</td>
<td>average layer diameter</td>
</tr>
<tr>
<td>$L_c$</td>
<td>average layer thickness</td>
</tr>
<tr>
<td>$L_{n,k,l}$</td>
<td>crystallite size</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
</tr>
<tr>
<td>$m_n$</td>
<td>neutron mass</td>
</tr>
<tr>
<td>NA</td>
<td>numerical aperture</td>
</tr>
</tbody>
</table>
\begin{align*}
n & \quad \text{neutron} \\
p & \quad \text{resonance escape probability} \\
p_e & \quad \text{perimeter of fitted ellipse} \\
P_{\text{FNLL}} & \quad \text{fast non-leakage probability} \\
P_{\text{TNLL}} & \quad \text{thermal non-leakage probability} \\
Q & \quad \text{binding energy} \\
Q_{\text{ex}} & \quad \text{excitation energy} \\
R_{p\theta} & \quad \text{radius of particle at angle } \theta \\
R_{\ell\theta} & \quad \text{radius of fitted ellipse at angle } \theta \\
S & \quad \text{surface area} \\
T & \quad \text{temperature} \\
u & \quad \text{atomic mass unit} \\
V & \quad \text{pulse velocity} \\
V' & \quad \text{volume} \\
V_T & \quad \text{transverse velocity} \\
V_L & \quad \text{longitudinal velocity} \\
v & \quad \text{velocity} \\
W & \quad \text{weight} \\
W' & \quad \text{width} \\
\beta & \quad \text{full width half maximum} \\
\beta_E & \quad \text{strain broadening} \\
\beta_L & \quad \text{size broadening} \\
\beta_{\text{tot}} & \quad \text{total line broadening} \\
\gamma & \quad \text{specific weight} \\
\varepsilon & \quad \text{strain} \\
\varepsilon_f & \quad \text{fast fission factor} \\
\varepsilon' & \quad \text{mean inhomogeneous strain} \\
\varepsilon^{\text{total}} & \quad \text{total strain} \\
\varepsilon^e & \quad \text{elastic strain} \\
\varepsilon^{pc} & \quad \text{primary creep strain} \\
\varepsilon^{sc} & \quad \text{secondary creep strain} \\
\varepsilon^{dc} & \quad \text{dimensional change strain}
\end{align*}
\( e_{th} \) thermal strain
\( e_{ith} \) interaction thermal strain
\( e_{idc} \) interaction dimensional change strain
\( \eta \) thermal fission factor
\( \theta' \) internal friction force
\( \vartheta \) orientation angle
\( \lambda \) wavelength of visible light
\( \mu \) elastic constant
\( \mu' \) attenuation coefficient
\( \nu \) Poisson’s ratio
\( \rho \) density
\( \sigma \) stress
\( \sigma_p \) prestress
\( \xi \) reduction of neutron energy per collision
\( \Sigma_a \) neutron absorption cross section
\( \Sigma_s \) neutron scattering cross section
\( \varrho \) apparent density
\( \varphi(z) \) radiant flux at distance z
\( \omega \) porosity
\( \omega_c \) critical porosity
Abstract

University of Manchester
Joshua Edward Logan Taylor
PhD
Investigating the effects of stress on the microstructure of nuclear grade graphite
12th December 2015

Graphite is used as a moderating material and as a structural component in a number of current generation nuclear reactors. During reactor operation stresses develop in the graphite components, causing them to deform. If significant numbers of graphite components were to fail in this manner, the material’s effectiveness as a neutron moderator will be reduced, and the reactor’s safe operation may be compromised. It is therefore important to understand how the microstructure of graphite affects the material’s response to these stresses.

Despite much research into the effects of stress on nuclear grade graphite, there remain gaps in our understanding of this process, and there are a number of frequently observed limitations in the current research. Many existing studies either focus on the bulk material, ignoring the important changes at the microlevel; or focus on residual stresses due to the lack of available in-situ data.

An experimental programme was designed to study stress-induced changes to the microstructures of Gilsocarbon and Pile Grade A graphite used in UK nuclear reactors. Particular focus was paid to the deformation of the pore structure, since graphite is highly porous and the porosity has a significant effect on the strength and structural integrity of the graphite components. A compression rig was used to simulate the build-up of operational stresses, during which confocal laser microscopy and X-ray tomography were performed to quantify changes to the pore structure at the microlevel; while X-ray diffraction was performed to study deformation of the crystal lattice and quantify the build-up of lattice strains. Pore properties of interest included pore area, surface area, volume, eccentricity, orientation, angularity and separation. Crystal lattice properties of interest included layer spacing, unit cell and crystallite size parameters, lattice strains and Bacon Anisotropy Factor.

The experimental and analytical techniques were designed to significantly enhance our current understanding of how graphite responds to stress, with each observation made using a novel technique or improving the effectiveness of existing techniques. These studies have enabled significant novel observations and discussions of the stress-induced deformation behaviour of nuclear grade graphite to be made.
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I am also grateful for the efforts of the rest of the staff involved with the Nuclear Graphite Research Group, including Prof. Barry Marsden, Dr Abbie Jones, Dr Marc Schmidt, Nicola Lawton and Susan Deighton. Their support, training and guidance ensured not just that I had access to all the resources I needed to successfully complete this project, but also that I had an enjoyable time doing it.

Special thanks go to the many postgraduates and postdoctoral scholars with whom I worked, including but not limited to Robert Worth, William Bodel, Maureen Haverty, Greg Black, David Arregui, Roxanne Neall, Olga Negri, Lorraine McDermott and Alex Theodosiou.

Lastly, I would like to thank my parents for providing me with considerable support during the completion of this project, and throughout my education as a whole.
Preface

For a nuclear reactor to operate efficiently, the materials used for each internal component must be selected with care. Each component of a nuclear reactor has a specific set of criteria that a potential material must fulfil in order to ensure safe and efficient operation. An unsuitable choice of material has the potential to result in the failure of the reactor; hence the properties of any materials considered for use in a nuclear reactor must be investigated in considerable detail before they are deemed suitable for use.

Graphite has prevailed for over 60 years as a nuclear material, and looks set to continue to do so for many decades further, particularly in the United Kingdom. This achievement emphasises the relevance and importance of graphite to the nuclear power industry. It also emphasises the importance of having a detailed understanding of the behaviour of graphite, particularly in response to the hostile conditions graphite moderator components must experience in current and future nuclear reactors.

In a graphite-moderated nuclear reactor, a variety of component stresses can build up. These stresses affect the material and microstructural properties of the moderator, and hence the bulk component behaviour is changed. The consequences of these behavioural changes depend on the type of stress, its magnitude and its location. It is therefore important to improve our understanding of how the material’s properties and behaviour change when stresses build up due to the harsh conditions in an operational nuclear reactor. Although some of these behaviours are well documented – if this were not the case then the material would not have been cleared for use – there are still characteristics that are not fully understood. Further research into these properties may yield useful information and allow a rethink into the way that graphite is utilised as a reactor component.

Graphite bricks in nuclear reactors cannot be repaired or replaced, which means that the structural integrity of the graphite bricks are one of the main factors that govern the operational lifetimes of the reactors. Therefore, research into how graphite responds to stress growth is predominantly relevant for life extension of existing reactors. Given that many of Britain’s graphite-moderated reactors are aging, and in some cases operating beyond their original designed lifespans, the integrity of graphite bricks is a major concern. Considerable amounts of time and money are being
dedicated to determining how much longer Britain’s graphite moderated reactor fleet can operate safely. Although there are currently no plans for further current generation graphite moderated reactors to be built in Britain, the research would also be relevant for maximising the operational lifetimes, efficiency and safety of next generation graphite moderated reactors.

At a time when there is considerable public debate about the merits of nuclear energy and opinions are divided on whether it has a future in both Britain and the wider world, ensuring the safe and efficient operation of nuclear reactors is integral to securing the future of nuclear power generation. Since aging graphite components represent one of the main concerns for the British nuclear industry, it was decided that a project to further our understanding of the behaviour of graphite should be performed. Therefore, the aim of this research project is to investigate the effects of stress on the material and microstructural properties of graphite that govern its operation as a moderator, with the intention of providing further insight into the suitability of aging graphite components in nuclear reactors. Three separate experimental techniques were selected for this study. Two imaging techniques were used – confocal laser microscopy and X-ray tomography, while the third technique, X-ray diffraction, enabled analysis of the crystal structure of graphite.

**Thesis Structure**

This thesis is split into seven chapters and one appendix.

Chapter 1 discusses the background to the project. The physical processes that underpin nuclear fission and how these processes occur in a nuclear reactor are introduced. The function of the neutron moderator and the use of nuclear grade graphite in this role are discussed. This is followed by an analysis of the structure and material properties of various grades of graphite, how they are manufactured, and a discussion of the growth of graphite-moderated nuclear reactors from the 1940s to next generation prototype reactors. Lastly, the research topic discussed in the Preface is placed into the context of the British nuclear power industry.

Chapter 2 contains a comprehensive literature review of research into the stress-induced behaviour of nuclear grade graphite. Basic models of deformation in graphite and the mechanisms that cause deformation in operational nuclear reactors
are introduced, followed by the discussion of a wide range of studies into the effects of stress on various material and microstructural properties of graphite. Flaws and gaps in the existing research and ideas for new experiments were analysed to produce a coherent and novel research programme designed to study the issues discussed in the Preface.

Chapter 3 discusses the machining, preparation and metrology that each graphite sample underwent before being used during the main experimental programme. The preparation required for each sample differed depending on the experimental technique it was to be used with. In addition, weight and size details are provided for each sample used during the project.

Chapters 4 – 6 each detail a different experimental technique and the associated data analysis. Three main experimental techniques were utilised during the project – the imaging techniques of confocal laser microscopy and X-ray tomography, and the crystal structure analysis technique of X-ray crystallography. These techniques are discussed in Chapters 4, 5 and 6 respectively. In each chapter the theoretical background of the technique is introduced, the experimental methodologies are described and the results of the experiments are shown and discussed in detail. At the end of each chapter, a Summary is provided that briefly describes the main results and the main novel techniques and analyses that differentiate this study from any other.

Chapter 7 contains the overall conclusions of the project. The successes and limitations of the project are analysed, the implications of the project for the British nuclear industry are discussed, and suggestions for future work are made.

Lastly, the Appendix discusses the various journal and book publications that have arisen from the research documented in this thesis.
Chapter 1: Introduction

This chapter discusses the theoretical background of nuclear power, the importance of graphite as a nuclear material, and the development of commercial nuclear power generation over the past 70 years. The problem of stress-induced deformation of graphite components, discussed in the Preface, is put into the context of the modern nuclear power industry, and a research programme to investigate this problem is introduced.

1.1 Nuclear Fission

A nuclear fission reaction requires the absorption of a free neutron into the nucleus of a nuclear fuel element. The addition of a neutron leaves the nucleus in an excited state and it becomes very unstable. Very quickly, the nucleus breaks down into a number of smaller nuclei and free neutrons. A typical example of a fission reaction using uranium-235 is shown in Equation (1.1) below:

\[ ^{235}U + n \rightarrow ^{236}U^{*} \rightarrow ^{147}La + ^{87}Br + 2n \]  

A uranium-235 nucleus absorbs a neutron, becomes excited and subsequently decays into lanthanum-147 and a bromine-87, accompanied by the emission of two free neutrons. The free neutrons are then absorbed into other uranium nuclei, resulting in a chain reaction that will reliably continue as long as there are sufficient free neutrons being produced, and sufficient fuel nuclei available.

During the reaction energy is conserved. Due to the difference in binding energy (the energy required to hold a nucleus together) between the parent nucleus and the daughter nuclei, a known amount of energy, \( Q \), is released during the reaction. Typically, the amount of energy released in a fission process is around 200 MeV.

Since such large amounts of energy are generated through the decay of heavy nuclei into lighter nuclei, one may assume that fission is a relatively probable process and that it may occur spontaneously. However, spontaneous fission is very unlikely and can only occur under specific circumstances. This is due to the strong interaction, a force which holds the protons and neutrons together in the nucleus. This force has a range of the order of a few femtometres \( (10^{-15} \text{ m}) \) and is attractive between hadrons.
Introduction

Beyond this range the strength of the strong interaction rapidly diminishes and the *Coulomb interaction*, a repulsive force between charged particles, becomes dominant. The behaviour of these forces at different ranges is shown in Figure 1.1.

![Graph showing the mechanisms of interaction between charged particles and the ranges at which the interactions operate. $B_c$ represents the Coulomb barrier.](image)

**Figure 1.1**: Graph showing the mechanisms of interaction between charged particles and the ranges at which the interactions operate. $B_c$ represents the Coulomb barrier.

In order for spontaneous fission to occur, there must be enough energy to separate the daughter nuclei beyond the range where the strong force dominates. To separate two nuclei, the energy release must be comparable to the Coulomb barrier shown in Figure 1.1. This is typically not the case for nuclear fuel nuclei, therefore the probability of it occurring is very low. It is worth noting, however, that spontaneous fission becomes non-negligible in certain very heavy isotopes (with mass number typically above 300). It can also occur through the quantum mechanical tunnelling effect, where the wave-nature of particles allows penetration through barriers that classical mechanics would forbid.

Since spontaneous fission is not typically feasible, it must be triggered. As shown in Equation (1.1), neutron absorption is used to excite the fuel nucleus so that it may overcome the Coulomb barrier. The advantage of using neutrons for this purpose is that neutrons have no charge, so they do not have to overcome the Coulomb barrier in order to be initially absorbed.

The energy required to induce fission is known as the *activation energy*. It is provided by the mass and the kinetic energy of the free neutron prior to absorption.
Considering the excitation process of uranium-235 shown in Equation (1.1), the excitation energy $Q_{ex}$ can be calculated using Equation (1.2):

$$Q_{ex} = \left[ m^{(^{236}U^*)} - m^{(^{236}U)} \right] c^2$$  \hspace{1cm} (1.2)

where $m$ represents the mass of the nucleus and $c$ is the speed of light in a vacuum.

If the excitation energy calculated using Equation (1.2) is greater than the activation energy required for fission, then fission can occur with a zero kinetic energy neutron. Otherwise, the neutron must have some amount of kinetic energy in order to induce fission. For the fission process in Equation (1.1), the excitation energy exceeds the fission energy by approximately 0.3 MeV, enabling a neutron to induce fission with no energy requirements.

### 1.1.1 Competing Processes with Fission

To maintain a successful chain reaction of fission processes, a sufficient number of neutrons must be generated in a single fission reaction to ensure that, on average, at least one further fission process can be induced and the reaction sustained. The neutron reproduction factor, $k$, is defined as the ratio between the number of neutrons present in one generation to the number of neutrons present in the preceding generation. If $k$ is equal to one, the number of neutrons will remain constant since each individual fission process leads to one further process. If $k$ is less than one, too few neutrons are being produced and the reaction will eventually cease. If $k$ is greater than 1, the neutron population will grow exponentially, with potentially dangerous consequences.

There are six distinct processes that affect the neutron reproduction factor that are defined by an equation known as the *six factor formula* [1]:

$$k = \eta f p \varepsilon_f P_{FNL} P_{TNL}$$  \hspace{1cm} (1.3)
Each term is discussed below:

- **The thermal fission factor, $\eta$:** This term represents the number of neutrons produced through fission, per neutron absorption by the fuel.

- **The thermal utilisation factor, $f$:** This term represents the probability that neutron absorption occurs in the fuel, rather than in any other component in the nuclear reactor.

- **The resonance escape probability, $p$:** This term represents the fraction of neutrons that are able to slow down to thermal speeds without encountering resonances in the fuel capture cross section and being absorbed.

- **The fast fission factor, $\epsilon_f$:** This term represents the ratio between the total number of neutrons released and the number of neutrons released by thermal fission processes.

- **The fast non-leakage probability, $P_{FNL}:** This term represents the probability that a fast neutron will not leak out of the system.

- **The thermal non-leakage probability, $P_{TNL}:** This term represents the probability that a thermal neutron will not leak out of the system.

In an operational nuclear reactor it is desirable to keep the neutron reproduction factor as close to 1 as possible. The design, materials and operating conditions of the reactor are carefully controlled to ensure that the neutron reproduction factor is kept as close as possible to this value.

However, nuclear fission is not the only process that may occur once a neutron has been absorbed into a fuel nucleus. For an excited fuel nucleus containing an absorbed neutron, there are three competing reactions that will not result in fission, thus removing available neutrons from the chain reaction process. These processes are elastic scattering, inelastic scattering and radiative capture, and are discussed in Table 1.1.
### Table 1.1: The four competing processes that may occur upon absorption of a neutron by a uranium-235 nucleus.

<table>
<thead>
<tr>
<th>Name</th>
<th>Process</th>
<th>Outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fission</td>
<td>$^{236}\text{U}^* \rightarrow ^{235}\text{U}^* + n$</td>
<td>Successful fission</td>
</tr>
<tr>
<td>Elastic Scattering</td>
<td>$^{236}\text{U}^* \rightarrow ^{235}\text{U} + n$</td>
<td>No change</td>
</tr>
<tr>
<td>Inelastic Scattering</td>
<td>$^{236}\text{U}^* \rightarrow ^{235}\text{U}^* + n$</td>
<td>Neutron loses energy, Uranium remains in excited state</td>
</tr>
<tr>
<td>Radiative Capture</td>
<td>$^{236}\text{U}^* \rightarrow ^{236}\text{U} + \gamma$</td>
<td>Energy release in the form of gamma ray</td>
</tr>
</tbody>
</table>

To sustain the nuclear chain reaction required for energy generation, nuclear fission must be the dominant process. For a given fissile material, the likelihood of each process occurring is strongly dependent upon the kinetic energy of the incident neutron. Figure 1.2 shows the variation of the cross-section of each of the four processes shown in Table 1.1 with the energy of the incoming neutron for a uranium-235 nucleus.

![Figure 1.2](image)

Figure 1.2: The relationship between cross-section and energy following neutron absorption by a uranium-235 nucleus. The processes shown are fission (n,f), elastic scatter (n,n), inelastic scatter (n,n') and radiative capture (n,γ) [2].

The nuclear fission cross-section is dominant only at low energies, so to maximise the likelihood of successful fission of uranium-235 it is necessary to ensure that the free neutrons have as little energy as possible upon absorption into the nucleus.

Fission of nuclear fuel produces neutrons with a mean energy of 2 MeV and a mean speed of around 20,000 km/s [3]. These are known as fast neutrons. Figure 1.2
shows that for a fast neutron interacting with a uranium-235 nucleus, elastic scattering is the dominant cross-section, followed by inelastic scattering. Nuclear fission has a relatively low probability of occurring, so fast neutrons are not suitable for fission of uranium-235.

A much less energetic classification of neutrons known as thermal neutrons have energies of around 0.025 eV, which is the mode of the Maxwell-Boltzmann distribution, a statistical model of freely moving particle speeds in a gas, at 290 K. Figure 1.2 shows that for thermal neutrons of this energy interacting with a uranium-235 nucleus, nuclear fission is the most likely outcome, since the fission cross-section is almost an order of magnitude larger than its nearest competing process. Therefore, thermal neutrons are well suited for fission with uranium-235, and in order for successful fission to occur, the neutrons must be slowed down from fast speeds to thermal speeds.

However, not every fissile isotope behaves in this manner. Figure 1.3 shows the cross-sections of competing processes for fission with a uranium-238 nucleus. In this case the fission process does not dominate at any energy scale, and only occurs at energies between 1 and 10 MeV. Therefore, uranium-238 can undergo fission using fast neutrons and does not require the neutrons produced during previous fission processes to be slowed down at all.

Figure 1.3: The relationship between cross-section and energy following neutron absorption by a uranium-238 nucleus. The processes shown are fission (n,f), elastic scatter (n,n), inelastic scatter (n,n') and radiative capture (n,γ) [2].
Energy $E$ of a neutron of mass $m$ and velocity $v$ is related to temperature $T$ by:

$$E = \frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

(1.4)

Where $k_B$ is the Boltzmann constant. Hence, to reduce the velocity of a fast neutron, energy must be dissipated from the particle to its surroundings. The simplest way to accomplish this is to force each neutron to undergo a series of scattering events, each transferring a portion of the neutron’s kinetic energy into a different medium, before interacting with the fuel. For this purpose a material known as a neutron moderator surrounds the fuel, its purpose being to reduce the speed of the neutrons, turning them into thermal neutrons prior to their absorption into the fuel.

1.2 The Neutron Moderator

1.2.1 Requirements of a Neutron Moderator

For a material to be considered a suitable moderator, it needs to fulfil four main criteria.

The first criterion is that the material must have a low atomic weight. Consider a scenario where an incoming fast neutron of mass $m_n$ and speed $v$ collides with a stationary moderator nucleus of mass $M$. After scattering the neutron recoils at velocity $v_1$ and the moderator nucleus at velocity $v_2$. Assuming that the neutron is scattered through 180°, the law of conservation of energy shows that:

$$\frac{1}{2}m_n v^2 = \frac{1}{2}m_n v_1^2 + \frac{1}{2}M v_2^2$$

(1.5)

$$v_2^2 = \frac{m_n}{M} (v^2 - v_1^2)$$

(1.6)

Conservation of momentum also shows that:

$$m_n v = M v_2 - m_n v_1$$

(1.7)
Combining these equations and solving for the ratio of final neutron velocity to initial neutron velocity:

\[
\therefore v_f^2 = \left(\frac{m_n}{M}\right)^2 (v + v_1)^2
\]  

(1.8)

Hence when \( M \gg m_n \), the neutron transfers very little energy to the moderator during the collision. In order to maximise energy transfer during collisions, which increases the likelihood of the neutron reaching thermal speeds before fission, low atomic mass moderating materials are desirable [4].

The second criterion requires the material to have a high moderating efficiency, defined as the ratio of neutron scattering cross section \( \Sigma_s \) to neutron absorption cross section \( \Sigma_a \), weighted by the reduction of neutron energy per collision \( \xi \), as defined by Equation (1.10) [5]. Absorption of neutrons by the moderator removes them from the fission chain reaction, so materials with high neutron absorption cross-sections are not suitable moderators.

\[
E' = \frac{\xi \Sigma_s}{\Sigma_a}
\]  

(1.10)

The six-factor formula describes the competing processes that may happen to a free neutron in a nuclear reactor. In order to maximise the efficiency of the moderating material, it must have a high neutron scattering cross-section and a low neutron absorption cross-section. Moderating efficiency, \( E' \), quantifies the ratio of these two processes.

The third criterion is that the material must be resistant to neutron damage and ionising radiation damage. Moderator components are precisely machined for their purpose. Excessive irradiation-induced damage may result in the components losing their structural integrity and becoming unsuitable for neutron moderation. It may also put the safe and efficient operation of the reactor at risk. Graphite components cannot typically be repaired or replaced once installed in a nuclear reactor, therefore any
potential moderating material needs to be resistant to damage for at least the duration of the reactor’s operating lifetime. If that is not possible, maximising the lifespan of the components is essential.

Lastly, the material should be readily available and relatively cheap, to ensure that the cost of commissioning the reactor is not prohibitively high and hence not profitable enough for an energy supplier to consider running the operation.

1.2.2 Moderating Materials

A variety of different materials are suitable for use as moderators. There is not one single material which provides the best solution for all four of the criteria discussed in Section 1.2.1, so a compromise is required. Table 1.2 shows some of the materials currently in use as moderating components in various designs of nuclear reactor.

<table>
<thead>
<tr>
<th>Moderator</th>
<th>Reactor Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light water</td>
<td>Pressurised Water Reactor (PWR), Boiling Water Reactor (BWR), Water-Water Energetic Reactor (VVER)</td>
<td>Relatively cheap, Hydrogen has low atomic weight (1.008 u)</td>
<td>Poor moderating efficiency, Requires enriched uranium due to low fission probability, Water cannot be used as a structural material</td>
</tr>
<tr>
<td>Heavy water</td>
<td>Canada Deuterium Uranium (CANDU)</td>
<td>High moderating efficiency, Hydrogen has low atomic weight (1.008 u)</td>
<td>Expensive</td>
</tr>
<tr>
<td>Graphite</td>
<td>Advanced Gas-Cooled Reactor (AGR), Magnox, High Power Channel-Type Reactor (RMBK), High Temperature Reactor (HTR)</td>
<td>Reasonable moderating efficiency, Can be used as a structural component, Easy to handle, Relatively cheap</td>
<td>Relatively high atomic weight (12.011 u)</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Research reactors, Material Test Reactor (MTR)</td>
<td>High moderating efficiency, Reasonable atomic weight (9.012 u)</td>
<td>Expensive, Toxic</td>
</tr>
</tbody>
</table>

Table 1.2: Comparison of existing nuclear moderating materials with the advantages and disadvantages of each.
There is a case for using each of the materials listed in Table 1.2 as a nuclear moderator. In the UK, graphite was the material chosen for use in early designs of nuclear reactor, and this initial investment and knowledge has led to graphite being the favoured moderating material in the UK to this day. The history of graphite-moderated nuclear reactors, and the reasons why graphite was chosen for use in the UK, is discussed in Section 1.6.

1.2.3 Graphite as a Moderating Material

Graphite satisfactorily fulfil the requirements discussed above. It is available relatively cheaply, is easy to handle, and is not a harmful substance. It has a reasonable moderating efficiency. However, the relatively high atomic weight compared to other candidate materials means graphite does not remove as much energy from the neutrons during each collision as the other materials discussed in Table 1.2. Despite this, it has proven to be a successful moderating material and is used in several designs of fission reactor around the world. Table 1.3 shows a brief summary of the various types of commercial graphite moderated reactors and their use.

<table>
<thead>
<tr>
<th>Name</th>
<th>Countries</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGR</td>
<td>UK</td>
<td>1976 -</td>
</tr>
<tr>
<td>Magnox</td>
<td>UK, Italy, Japan</td>
<td>1956 -</td>
</tr>
<tr>
<td>RBMK</td>
<td>Russia</td>
<td>1954 -</td>
</tr>
<tr>
<td>HTR</td>
<td>UK, USA, Japan, China, Germany</td>
<td>1960s -</td>
</tr>
<tr>
<td>UNGG</td>
<td>France</td>
<td>1956 - 1994</td>
</tr>
</tbody>
</table>

Table 1.3: The main types of graphite moderated nuclear reactor used for power generation, countries in which they are most commonly used and their dates of operation.

1.3 Structure and Material Properties of Graphite

Graphite is one of many allotropes of carbon and can be found naturally in metamorphic rocks, igneous rocks and meteorites. Since the fourth millennium BC,
when the tendency of graphite to leave marks when rubbed on different surfaces was first observed and utilised to decorate pottery in the Neolithic period [7], graphite has been used to draw and write. The unique set of properties of graphite have rendered it useful for a variety of other purposes – for example, its electrical conductivity makes it a common component in batteries, while its low neutron absorption and high scattering cross sections render it a viable moderator in a nuclear fission reactor.

As shown in Figure 1.4, graphite has a layered planar structure. Carbon atoms are arranged in layers in a hexagonal lattice and commonly exhibit an ‘A – B – A – B...’ repeating structure, i.e. with two layers alternating between one another; while some naturally occurring grades of graphite exhibit an ‘A – B – C’ repeating arrangement. Identical layers are separated by 0.67 nm, known as the \textit{c-spacing}, while individual atoms are separated from their nearest neighbours by 0.14 nm. The \textit{a-spacing}, which defines the dimension of the unit cell parallel to the lattice planes, is known to be 0.25 nm, as shown in Figure 1.4 [8]. The unit cell for graphite, the simplest repeating structure in the crystal, is shown in Figure 1.5.

In a single layer the carbon atoms are held together by strong, short range covalent forces, while the layers themselves are held together by weak Van der Waals forces. This gives graphite its softness and allows layers to be removed with relative ease. The latter property explains why graphite is ideal for writing and drawing – rubbing graphite against a suitable material will remove the weakly bonded surface layers and transfer them to the other material – and has enabled the production of graphene, which is a single-atom thick slice of graphite. The covalent bonds holding atoms together within the planes, however, are much stronger. The breaking of these bonds will fundamentally alter the properties of bulk graphite and can have adverse effects on its performance as a nuclear moderator.
Figure 1.4: The hexagonal lattice structure of graphite [9].

Figure 1.5: The unit cell of the hexagonal lattice is shown in bold [8].

Another consequence of the planar structure of graphite is that the properties of the bulk material tend to be anisotropic, i.e. the properties will differ depending on the direction being examined. For example, phonons can travel quickly along planes but are less efficient when traversing between planes. This means that thermal and electrical conductivity of the material will vary depending on the direction being considered. These properties arise due to the preferred orientation in the crystal lattice and the preferred orientation of the pore structure with the graphite. However, the
degree of anisotropy can vary greatly between different grades of graphite. The manufacturing process detailed in Section 1.4, during which the raw materials are graphitized and purified, can influence the degree of anisotropy in the end product.

1.4 Preparation of Nuclear Grade Graphite

Due to the presence of significant levels of impurities, such as hydrocarbons and metals including silicon, iron and vanadium, naturally occurring graphite is not immediately suitable for use as a moderating component in a nuclear reactor. Before they can be used, they must undergo a manufacturing process designed to provide a product which satisfies the stringent requirements of a nuclear moderator – low impurity, low neutron absorption cross-section, high moderating efficiency and suitable strength to survive the physical conditions in an operational reactor. A typical method of manufacturing reactor grade graphite is shown in Figure 1.6.
Most commercially manufactured carbons contain two distinct components – a carbonaceous filler material and a binder to bond the filler material together.

Multiple filler materials are suitable for graphite manufacturing. Produced as a by-product of crude oil cracking, petroleum coke is easily graphitizable and can achieve a high degree of crystallinity when heated to 3000°C [10], making it a suitable filler material. Alternatively, pitch coke produced from coal tar, a by-product of coke production, can be used as a filler material [11]. Asphalt coke can also be used as a filler material when manufacturing graphite, though this is less common [12].

Coal tar pitch is the viscous residue produced during distillation of coal tar. It is commonly used as the binder material in graphite manufacturing due to its low cost,
high carbon content and its thermoplasticity – it is a solid at room temperatures but becomes a fluid at higher temperatures [13].

The first stage of the production process is to heat the raw petroleum coke to 1300°C to shrink the filler material and remove any remaining volatile hydrocarbons, in a process known as ‘calcination’. After cooling, around 25% of the weight of the coke has been lost [10] and the volume has decreased significantly. This is important because if such shrinkage were to occur after baking, later in the manufacturing process, it may break the bonds between the coke and the pitch, producing a weak and brittle graphite. Additionally, volatile hydrocarbons escaping during the baking process would cause disruptive forces, again leading to a brittle end product.

After calcination, the coke is milled and sized. Oversized components are crushed to produce particles ranging in size from a centimetre to a fraction of a millimetre. The finer material is milled into a ‘flour’ with a typical grain diameter of 250 µm [14], and the coke and flour are prepared for mixing.

The three individual components – coke, coke flour and pitch – are then mixed together and extruded or moulded into a material known as the ‘green body’. Varying the exact quantities of each component and the manufacturing process can result in graphite with significantly different structures and properties (discussed further in Section 1.5).

The green body is slowly heated to 500°C, releasing volatile gases in a process known as ‘baking’. Heating must be gradual to ensure that the gas does not escape too quickly, potentially damaging the structure [10]. A large amount of hydrogen is produced when the pitch pyrolyzes, allowing polymerization to occur and inducing cross-linking between the coke and pitch. As the heating process continues up to 1000°C, the carbon body becomes hard and brittle, but at this stage it still lacks the crystalline structure associated with graphite [8].

This ‘baked article’ is highly porous, so the carbon is impregnated to reduce the porosity and increase the bulk density. The impregnating fluid will enter the pores and, following subsequent re-baking or graphitisations, will deposit secondary carbon [10]. Coal tar pitch is commonly used as an impregnation fluid. This is often a different type of coal tar pitch to that used as a binder material - some of the heavier fractions present in the binder pitch are not present in the impregnation pitch [10]. The
impregnation process may need to be repeated several times in order to fill as many pores as possible.

The final stage in the manufacturing process is ‘graphitisation’, at which point the crystalline structure and long range order are developed and the remaining hydrogen is removed. The carbon is heated in a furnace – typically an Acheson or a Castner furnace. As the carbon is heated to 1500°C most of the hydrogen has been evolved, and by 2500°C the majority of the crystal growth has occurred [10]. The heating process typically takes up to four days, after which the material requires up to ten days to cool. The resulting material is nuclear grade graphite, possessing the crystalline structure and properties required for use in a nuclear reactor.

However, for certain operations further purification may be required, for example use in a graphite moderated breeder reactor [15]. Three common purification methods are [10]:

- Purification of the raw materials before the graphite production process begins.
- Further thermal purification, where the graphite is heated to a suitably high temperature to cause the impurities to diffuse out of the graphite.
- Chemical purification using halide salts or a gas containing halides.

Thermal purification is often the cheapest option but does not fully remove impurities, while chemical purification is the most effective but most expensive purification method. Raw material purification provides an acceptable compromise between cost and effectiveness and, as such, was used to produce nuclear grade graphite in Britain.

1.5 Grades of Graphite

There are many different types of graphite being used in nuclear reactors, and this project considers two of these: Pile Grade A (PGA) graphite and Gilsoarbon graphite. These grades of graphite were selected for study because they are both currently used in nuclear reactors in the UK.

1.5.1 Pile Grade A

PGA graphite, as used in British Magnox reactors, is an anisotropic grade of graphite. It consists of two distinct components – a carbonaceous filler phase suspended in a coal tar pitch binder phase. It is the filler phase that is predominantly
responsible for the anisotropic behaviour of the material. The filler particles, and the pores within them, have a large aspect ratio, meaning they are elongated in one axis. This axis is known as the major axis of the particle. Typically the minor axes - width and height - are of a similar dimension. During the manufacturing process the graphite undergoes an extrusion process to form the graphite into a geometry that is suitable for use in a nuclear reactor, and this process aligns the filler particles parallel to the extrusion direction [10]. The c-axis (see Figure 1.4) is oriented perpendicular to the long axis of the filler particles. No preferential orientation is observed in the binder phase.

Porosity in the filler particles takes the form of high aspect ratio, needle-like pores that are predominantly oriented parallel to the long axis of the filler particles. Thus the extrusion that occurs during the PGA manufacturing process also produces a large number of high aspect ratio, directionally aligned pores. The pores in the binder regions, however, exhibit no preferential orientation.

Figure 1.7 shows the surface of a Pile Grade A graphite sample. Some important features are identified.

Figure 1.7: Microscopy image showing the microstructure of PGA graphite. A few filler particles are highlighted. The preferential alignment of the filler particles from the top to the bottom of the image, i.e. along the extrusion direction, is visible.

1.5.2 Gilsocarbon

Gilsocarbon is produced by refining Gilsonite pitch which occurs naturally in Utah in the USA. Gilsocarbon contains the same basic features as PGA – a carbonaceous filler phase suspended in a pitch binder matrix, but the morphology of
these features gives the bulk material significantly different properties to PGA graphite. Gilsonite coke contains spherical, layered filler particles with a typical diameter of 1 mm [16]. During production, the Gilsonite is moulded rather than extruded, resulting in a random distribution and orientation of coke particles. The shape of these particles and the crystallites within them leads to a small degree of anisotropy in the bulk material. This degree of anisotropy is much smaller than in other grades of nuclear graphite, including Pile Grade A graphite, hence Gilsocarbon can be considered to be quasi-isotropic.

Porosity in the filler particles tends to take the form of very high aspect ratio pores that travel circumferentially around the particles, as shown in Figure 1.8. Pores in the binder phase have no preferential orientation. The end result is a grade of graphite that can be considered quasi-isotropic, with no directionality developing from the raw material or as a result of the manufacturing process. Figure 1.8 shows the surface of a sample of Gilsocarbon with the important features identified.

Figure 1.8: Microscopy image showing the microstructure of Gilsocarbon. Spherical filler particles are clearly visible, as well as significant porosity.
1.5.3 Comparison of the Material Properties of PGA and Gilsoarbon

Table 1.4 quantifies some of the important material properties of PGA and Gilsoarbon graphite [17]. Due to the varying degrees of anisotropy present in the graphite, certain material and microstructural properties will vary depending on the direction in which they are being measured. Therefore, specific orientations of bulk graphite are defined in terms of the extrusion direction, discussed in Section 1.4. This property is also known as the *grain direction*. Measurements made parallel to the extrusion direction are referred to as *with grain* (WG), while measurements made perpendicular to the extrusion direction are referred to as *against grain* (AG).
### Table 1.4: Some of the important material properties of PGA and Gilsocarbon. The anisotropy of PGA graphite results in different properties parallel and perpendicular to the extrusion/grain direction. These values are defined as WG (with grain) and AG (against grain). Data adapted from Brocklehurst and Kelly [17].

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Pile Grade A</th>
<th>Gilsocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g cm(^{-3})</td>
<td>1.74</td>
<td>1.81</td>
</tr>
<tr>
<td>Open pore volume</td>
<td>-</td>
<td>0.198</td>
<td>0.11</td>
</tr>
<tr>
<td>Closed pore volume</td>
<td>-</td>
<td>0.01</td>
<td>0.086</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>K(^{-1})</td>
<td>WG 0.9 \times 10(^{-6})</td>
<td>4.3 \times 10(^{-6})</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W m(^{-1}) K(^{-1})</td>
<td>WG 200</td>
<td>131</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>GPA</td>
<td>WG 11.7</td>
<td>10.85</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>WG 17</td>
<td>17.5</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>MPa</td>
<td>WG 19</td>
<td>23.00</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>MPa</td>
<td>WG 27</td>
<td>70.0</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>-</td>
<td>WG 0.07</td>
<td>0.21</td>
</tr>
<tr>
<td>Resistivity</td>
<td>(\mu) \Omega cm(^{-1})</td>
<td>WG 620</td>
<td>900</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>-</td>
<td>13.6 \times 10(^{-3})</td>
<td>3 \times 10(^{-3})</td>
</tr>
<tr>
<td>Viscous flow coefficient</td>
<td>(B_0) m(^2)</td>
<td>WG 712 \times 10(^{-16})</td>
<td>6.5 \times 10(^{-15})</td>
</tr>
<tr>
<td>Slip flow coefficient</td>
<td>(K_0) m</td>
<td>WG 108 \times 10(^{-9})</td>
<td>5.8 \times 10(^{-9})</td>
</tr>
</tbody>
</table>

Intr
1.6 Graphite-Moderated Reactors in the United Kingdom

Since construction began on Calder Hall (the UK’s first commercial nuclear reactor) in 1953, 14 separate nuclear power stations have generated energy for the national grid in the UK. Each site contained between one and four reactors, with all but one reactor being graphite moderated. There have been two designs of graphite moderated reactors used for commercial power generation in the UK – the Advanced Gas-cooled Reactor (AGR) and the Magnox reactor. The sole non-graphite moderated reactor is the Sizewell B Pressurized Water Reactor (PWR) which uses water as a moderating material. Table 1.5 provides details of each nuclear reactor used for commercial power generation in the UK.

The data in Table 1.5 shows the changes in the UK’s nuclear energy programme over time, from favouring Magnox reactors to favouring Advanced Gas-cooled Reactors. It also demonstrates the country’s reluctance to invest in the non-graphite moderated reactors, despite these being popular in mainland Europe and America.

Sections 1.6.1-1.6.4 discuss in more detail the evolution of the UK’s commercial nuclear power programme, the development of the graphite-moderated reactors that the UK relies on for energy, and the possible roles of graphite in next-generation nuclear reactor designs.
<table>
<thead>
<tr>
<th>Plant</th>
<th>Reactor</th>
<th>Type</th>
<th>Status</th>
<th>Startup</th>
<th>Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkeley</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>12 Jun, 1962</td>
<td>31 Mar, 1989</td>
</tr>
<tr>
<td>Bradwell</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Jul, 1962</td>
<td>31 Mar, 2002</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>12 Nov, 1962</td>
<td>30 Mar, 2002</td>
</tr>
<tr>
<td>Calder Hall</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Oct, 1956</td>
<td>31 Mar, 2003</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Feb, 1957</td>
<td>31 Mar, 2003</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 May, 1958</td>
<td>31 Mar, 2003</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Apr, 1959</td>
<td>31 Mar, 2003</td>
</tr>
<tr>
<td>Chapelcross</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Mar, 1959</td>
<td>29 Jun, 2004</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Aug, 1959</td>
<td>29 Jun, 2004</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Dec, 1959</td>
<td>29 Jun, 2004</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Mar, 1960</td>
<td>29 Jun, 2004</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>30 Dec, 1965</td>
<td>31 Dec, 2006</td>
</tr>
<tr>
<td>Dungeness B</td>
<td>1</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1985</td>
<td>2018</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2018</td>
</tr>
<tr>
<td>Hartlepool</td>
<td>1</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2024</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2024</td>
</tr>
<tr>
<td>Heysham 1</td>
<td>1</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2019</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2019</td>
</tr>
<tr>
<td>Heysham 2</td>
<td>1</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2023</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>AGR</td>
<td>Operational</td>
<td>01 Apr, 1989</td>
<td>2023</td>
</tr>
<tr>
<td>Hinkley Point A</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>30 Mar, 1965</td>
<td>23 May, 2000</td>
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<td>Shutdown</td>
<td>05 May, 1965</td>
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<td>2023</td>
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<td>2023</td>
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<td>2023</td>
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<td>AGR</td>
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<td>03 Feb, 1989</td>
<td>2023</td>
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<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>24 Mar, 1965</td>
<td>06 Feb, 1991</td>
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<tr>
<td>Wylfa</td>
<td>1</td>
<td>Magnox</td>
<td>Shutdown</td>
<td>01 Nov, 1971</td>
<td>30 Dec, 2015</td>
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Table 1.5: A list of nuclear reactors that are, or have been, operational in the UK. Reactors with a shaded background are still operational at the time of writing, and the closure dates are current best estimates.
1.6.1 Early Graphite-Moderated Reactors

The utilisation of fission for commercial energy generation has its roots in World War Two. By this point nuclear transmutation – the conversion of one element into another – was a well established technique. Having been first accomplished through conversion of nitrogen to oxygen by Ernest Rutherford in 1917, Enrico Fermi developed the technique to achieve nuclear fission. In 1934 Fermi bombarded uranium with neutrons and observed the creation of elements containing 93 and 94 protons. Fermi named these new elements *ausonium* and *hesperium* – now known as *neptunium* and *plutonium* respectively.

With nuclear fission successfully accomplished, thought turned to the creation of a sustainable fission chain reaction that could yield vast amounts of energy – with the applications in energy generation and nuclear weaponry both being considered. Fermi and Leo Szilárd proposed the idea of a nuclear pile, inside which a fission chain reaction could be maintained. Natural uranium was proposed as the fuel. The relative efficiencies of fast and thermal neutrons for fission processes were understood, so a graphite moderator was proposed to convert the population of fast neutrons into thermal neutrons.

In 1942 Fermi and Szilárd built *Chicago Pile-1*, the world’s first artificial nuclear reactor capable of sustaining a chain reaction. It was based upon their initial designs, with uranium fuel and a graphite moderator. However, it lacked many components that are standard in modern nuclear reactors, such as coolant and radiation shielding. Having successfully created a sustainable fission reactor, and with the United States now an active participant in the Second World War, focus turned to developing the technique of nuclear fission for use as a weapon. The Manhattan Project was formulated with the intention of producing the world’s first atomic bombs. A second graphite-moderated reactor, the *X-10 Pile*, was built at Oak Ridge National Laboratory in Tennessee and was used to breed plutonium-239 for use in the Trinity Test, the first successful detonation of a nuclear weapon.

Following the detonation of nuclear weapons in Japan and the conclusion of the Second World War, there was a shift in the way graphite was used in fission processes. In the US many of the existing reactors, including the *X-10 Pile*, were repurposed for peaceful programmes such as isotope production for medical and research purposes.
Meanwhile, other countries began producing graphite moderated reactors with the intention of starting their own nuclear weapons programmes to rival that of the US. This included Allied countries who had contributed to the Manhattan project, but found themselves shut out as the US ceased sharing their nuclear knowledge, for fear of other countries developing nuclear weapons.

In the UK, the Graphite Low Energy Experimental Pile (GLEEP) was built in 1947. It was the first operational reactor in Western Europe and was initially used for optimising reactor design and operation, and later for calibration of instruments for neutron flux measurement. This was followed by the graphite moderated British Experimental Pile-0 (BEPO) reactor, a research reactor built in 1948. In 1950 the graphite moderated Windscale Piles were constructed for the fabrication of plutonium for use in nuclear weapons.

Meanwhile, the USSR had been working on their own nuclear programme. Having acquired information about the Manhattan Project through espionage, most notably from Klaus Fuchs who worked at Los Alamos during the Second World War, the USSR’s initial reactors were based upon the American graphite moderated designs. In 1946 the F-1 Pile (also known as Soviet Pile 1) was built in Moscow. Using a graphite pile, it was built as a research reactor with a power level of 24 kW. It is still operational today.

While the construction of nuclear reactors for fabrication of materials for nuclear weapons continued into the 1950s, this decade also saw the development of nuclear power plants for electricity production. Obninsk Nuclear Power Plant, the first reactor in the world to be connected to a civilian power grid, was built in 1954 in the USSR and was graphite moderated. However, this reactor could not deliver electricity in commercial quantities. The first reactor to deliver significant amounts of electricity to the national grid was Calder Hall, built in the UK in 1956. Calder Hall was graphite moderated and the reactor had a novel design that became known as a Magnox reactor.

1.6.2 The Magnox Reactor

The Magnox reactor design was originally created to breed plutonium for use in nuclear weapons for the United Kingdom. It was observed that the large amounts of
heat produced as a by-product of the plutonium production process could be harnessed for commercial energy production, and in 1956 the Magnox reactor at Calder Hall was connected to the national grid.

The name ‘Magnox’ is derived from the predominantly magnesium and aluminium alloy used to clad the uranium metal fuel components to stop them oxidising. Graphite is used as the moderator and carbon dioxide as the coolant. The uranium fuel itself is unenriched. Figure 1.9 shows a schematic of the Magnox reactor design.

![Schematic of a Magnox reactor.](image)

At the time, the Magnox reactor’s main competition was the water cooled reactor, which was being embraced by the US. However, the Magnox reactor design had a few advantages over its water-cooled rivals:

- The moderator had a particularly low neutron capture cross-section, as discussed in Section 1.2.1, allowing a high moderating efficiency.
- The use of uranium metal fuel rather than uranium oxide made reprocessing easier, safer and cheaper.
- Gas-cooled reactors were expected to become more efficient over time as inert coolants became viable. By comparison, water-cooled reactors were already
acting close to their maximum temperature, which is governed by the triple point of water [18].

However, there were a significant number of drawbacks in the design that eventually led to the demise of the Magnox reactor:

- The magnesium and aluminium cladding had a low melting point, limiting the temperature that the reactor could operate at, meaning that much larger reactors were required to produce the amount of energy equivalent to that of a water-cooled reactor.
- Low coolant heat transfer capacity also required that the reactors be much larger than water reactors to produce the same amount of energy.
- Uranium metal has a low autoignition temperature such that it may spontaneously ignite if exposed to air during reactor operation.
- The fuel cladding material reacted with water, preventing the storage of spent fuel in water, one of the most common methods of storing used fuel at the time.
- The use of uranium metal for the fuel (as opposed to uranium oxide) required faster reprocessing of fuel. This problem necessitated the construction of dedicated reprocessing facilities in the UK.

As Table 1.5 shows, all but one of the twenty-six Magnox reactors built in the UK have now shut down. The considerable drawbacks with the Magnox design, coupled with the significant advances in nuclear power generation in the 1970s and 1980s, led to the Magnox design falling out of favour in the UK. After a long period in the 1970s with no further construction of nuclear reactors, an improved design of nuclear reactor was introduced, known as the Advanced Gas-Cooled Reactor.

1.6.3 The Advanced Gas-Cooled Reactor

The Advanced Gas-Cooled Reactor is a second generation nuclear reactor that exhibits a number of improvements and advantages over its first generation counterparts. Like the Magnox reactor, the AGR is graphite moderated, cooled by carbon dioxide and fuelled by uranium. However, the main advantage of the AGR
design is that it can operate at much higher temperatures – up to around 650° - which allows a greater thermal efficiency. The disadvantage of the higher temperatures is that the fuel requires stainless steel cladding to resist the temperatures. This material has a higher neutron capture cross section than the magnesium and aluminium alloy used to clad the fuel in Magnox reactors, so the uranium fuel must be enriched to compensate. Enrichment is a process that increases the proportion of uranium-235 nuclei in the fuel compared to uranium-238, and is performed due to only the former isotope being suitable for fission by thermal neutrons, as shown in Figure 1.2 and Figure 1.3.

Cylindrical enriched uranium pellets are collected into groups of 20 and are inserted into thin cylindrical fuel rods. Groups of 36 fuel rods are collected into a circular array known as an assembly, and each assembly is placed into a channel cut through the centre of a graphite moderator brick. Figure 1.10 shows the structure of a fuel assembly, while Figure 1.11 shows a cross-sectional schematic of an AGR.

Figure 1.10: Cutaway of an AGR fuel assembly. Each assembly contains a circular array of 36 fuel rods, each of which contains 20 enriched uranium oxide pellets. Each assembly is surrounded by a graphite sleeve [19].
In the late 1970s and early 1980s, AGRs started to operate in the United Kingdom. The greater energy output, increased efficiency and more economically viable design meant that the older Magnox designs were rapidly becoming obsolete. No further Magnox reactors were built after the first AGR started operating.

By 1990 all of the 14 AGRs currently operating in the United Kingdom had been built, and shortly afterwards the decommissioning started on some of the older Magnox reactors. This continued over the next two decades so that only one Magnox reactor, Wylfa reactor 1, is still operational. Although nuclear power was proving sufficiently reliable and safe for energy generation in the UK, only one new nuclear power plant – a Pressurised Water Reactor (PWR) at Sizewell B – was built to replace the Magnox reactors as they were being shut down. The expected lifetimes for the current AGRs vary from the late 2010s to mid 2020s, as shown in Table 1.5.

There are currently no plans to build any new AGRs in the UK. Two new reactors to be built at Hinkley Point C will use the PWR design instead.

1.6.4 Next-Generation Graphite Moderated Reactors

Generation IV reactors are a class of mostly theoretical reactors which are currently being researched. A few operational prototypes currently exist, with the
anticipation of construction for commercial use commencing in the 2030s or 2040s. They are being designed to use emerging technologies to address specific limitations with current generation reactors, with major targets including maximising economic safety and viability, and minimising waste. Graphite is a candidate moderator material for a number of theoretical next-generation reactor designs.

The *Very High Temperature Reactor* (VHTR) is a reactor concept that uses a graphite moderator, helium as the coolant and uranium as the fuel. Two separate configurations of fuel and moderator are proposed:

- A *pebble bed reactor* (PBR) consists of spherical fuel pellets coated in silicon carbide (SiC). Groups of thousands of pellets are embedded in a graphite ‘pebble’ the size of a tennis ball, which acts as the moderating material. New pebbles can be inserted, and old pebbles removed from the core over time. Fission processes release energy that heats a gas coolant, which in turn heats a separate fluid used to drive turbines.

- A *prismatic block reactor* (PMR) again comprises of spherical fuel pellets coated in silicon carbide. However, in this design the fuel pellets also have a series of thin layers of carbon applied to them. An inner layer of porous carbon captures fission products emitted from the fuel, while the subsequent layers of pyrolytic carbon provide structural support. The pellets are set into hexagonal blocks of graphite, which provide the moderation. These graphite blocks are stacked to fit into a pressure vessel.

The *Molten Salt Reactor* (MSR) is a reactor concept that uses a molten salt mixture as the coolant and, in some cases, also as the fuel. The advantage of this design is that the reactor can run at very high temperatures, for high efficiency, whilst maintaining low pressures. A pyrolytic graphite is used as the moderator, and the configuration of the graphite components depends on whether the fuel is a solid or a liquid. In both cases, the graphite core is made of large blocks. However, solid ceramic fuels are suspended in the graphite matrix, while liquid fuels are dissolved in the coolant. Thus, liquid fuels can travel throughout the reactor, but only become critical once inside the graphite core.
Although generation IV reactor designs are mostly still at the theoretical stage, graphite remains the most likely material to be used as the moderator in some of these designs.

1.7 Conclusions and Research Objectives

There has been considerable investment into graphite moderator components over the past 60 years, particularly in the UK. With only one nuclear reactor currently operating that is not graphite moderated, the importance of the material to the UK’s nuclear industry cannot be understated.

In an operational nuclear reactor, a number of mechanisms exist that generate stresses in graphite components. These mechanisms include irradiation damage, thermal discontinuities between different regions within the material, and dead weight of reactor components. These stresses have a significant effect on the operational lifetimes of nuclear reactors. Since graphite bricks cannot be repaired or replaced, the structural integrity of the graphite bricks are one of the main factors that govern the operational lifetime of the reactors.

It is important to ensure that the reactors are operating safely and efficiently, and this may conflict with the desire to keep the aging plants operational for as long as possible. This issue is worsened by the lack of any new nuclear reactors being opened in Britain since 1995. To satisfy energy demand, reactors are being kept operational well beyond their original anticipated lifetimes. Aging reactor components suffer from structural degradation, and the longer a component is exposed to the working conditions in an operational nuclear reactor, the more damaged and degraded the component will become. If many bricks were to fail in this manner, it may compromise the safety and the efficiency of the reactor. It is important to have a detailed understanding of how graphite reactor components respond to stress build-up during reactor operation and to be able to estimate how long the reactor can safely function, before components become too damaged.

Therefore, a research project is proposed to investigate the effects of stress on the material and microstructural properties of graphite that govern its operation as a moderator, with the intention of providing further insight into the sustainability of aging graphite components in nuclear reactors.
Since graphite is well established as a nuclear material, many studies into the microstructural behaviour of graphite already exist. Before proposing a research programme for this investigation, a detailed study of the existing literature documenting our current understanding of the behaviour of graphite has been conducted. Particular attention was afforded to the flaws and gaps in the existing research, with the intention of formulating a novel and coherent series of experiments and analyses to extend and enhance our current understanding of the response of graphite to stresses. This literature review is documented in Chapter 2.
Chapter 2: Literature Review

In order to propose an experimentally valid, novel series of experiments, it is important to establish a clear picture of the existing research in the field. Therefore, a literature review has been undertaken. Since graphite is such an important nuclear material, particularly in the UK, there is a considerable amount of existing literature discussing it in the context of nuclear power generation. However, this literature is not comprehensive, and there are gaps in the current understanding of the behaviour of nuclear graphite.

A wide variety of research papers, books and theses have been consulted to evaluate the current body of knowledge into the effects of stress on graphite. Of particular interest are documented difficulties, major methodological flaws, conflicting results and gaps in the existing research. The identification of these form the basis of a research project that will yield useful and novel results; and potentially extend our knowledge of graphite as a nuclear material.

Section 2.1 discusses the current understanding of the deformation behaviour and resulting variation of Young’s modulus and porosity in graphite, and the effects of radiation on the crystal structure of graphite. These fundamental properties have already been studied in great detail, and need to be understood before stress-induced changes can be considered.

Section 2.2 discusses the research into stress-induced changes in the material properties of graphite, with a particular focus on the variation of Young’s modulus and porosity. Two research groups are of particular interest in this area of research. The first group is the Japanese Atomic Energy Research Institute, who undertook a number of experiments between 1964 and 1998 on how stress affects the material properties of graphite, in particular the Young’s modulus. The second group is the Nuclear Graphite Research Group at the University of Manchester, one of a small number of groups in the UK dedicated to the study of nuclear graphite.

Section 2.3 looks at studies that have attempted to link the material in Sections 2.1 and 2.2 together by considering the relationship between porosity and Young’s modulus.

---

1 The Japanese Atomic Energy Research Institute merged with the Japan Nuclear Cycle Development Institute in 2005 to become the Japan Atomic Energy Agency.
Lastly, Section 2.4 contains the conclusions from the literature study. Consistencies and conflicts in results and methods across all of the relevant research are discussed, gaps and flaws in the existing research are identified, and from these conclusions a novel experimental program is proposed.

2.1 Studies into the Fundamental Material Properties of Graphite

2.1.1 Young’s Modulus and Deformation in Graphite

Graphite is well known for being a brittle solid. It exhibits non-linear deformation behaviour, as shown in the stress-strain relationship in Figure 2.1. Two distinct values of Young’s moduli can be defined for this behaviour. The *dynamic Young's modulus* is typically calculated using vibratory conditions (such as force vibration testing), while the *static Young’s modulus* can be derived from deformation experiments.

The Young’s modulus of the material, the ratio of stress, $\sigma$, to strain, $\varepsilon$, and hence the gradient at a specific point on the curve in Figure 2.1, decreases with increasing applied force [21]. Since the data in Figure 2.1 was from a compressive loading experiment, suitable values of the static Young’s modulus can be calculated. When the applied force is fully removed, the graphite does not fully recover and exhibits permanent deformation. The material also exhibits hysteresis, in that the loading and unloading curves do not coincide with each other [18].
Jenkins [21] studied the relationship between stress and strain in nuclear grade graphite. He attempted to explain the behaviour displayed in Figure 2.1 using an analogy of equally spaced friction blocks with backing springs to represent the structure of graphite (graphite is envisioned as a lattice of carbon atoms surrounding the filler grains). As the external force exerted on the structure increases, the blocks will move further from their neutral positions. The springs will transfer, but also dampen, this effect to neighbouring blocks. Upon removal of the applied stress, a block will only return to its original position if the stored energy in the backing springs can overcome the friction force of the block plus the applied stress.

This model predicts the initial stress-induced behaviour as:

$$\varepsilon = A'\sigma + B'\sigma^2$$  \hspace{1cm} (2.1)

where $A'$ is the elastic compliance, the inverse of the Young's modulus; and $B'$ is an elastic constant. The first term in this equation is the Hookean component (the springs), while the second term is the Voigt element (the friction blocks) [21]. Jenkins suggested that, based on this model, the strain experienced by a single grain, $\varepsilon$, can be defined as:
\[ \varepsilon = \frac{k(\sigma - \theta')}{\mu} \]  \hspace{1cm} (2.2)

where \( \sigma \) is the applied force, \( \theta' \) is the internal frictional force of the friction block, \( \mu \) is the elastic constant of the springs and \( k \) is a constant.

This model is very basic, and makes a number of simplifications and approximations regarding the structure of graphite. For example, it assumes that the material is homogeneous and isotropic. The model also assumes that the stress-strain behaviour of graphite is governed predominantly by the crystal structure, when the effects of porosity are now known to have a significant effect on the material. Despite these limitations, the model works well at low stresses but was observed to become less accurate at higher stresses. Jenkins proposed that this deviation from the model at high stresses is due to an increased density in micro-cracks reducing the apparent modulus.

Cottrell [22] proposed a similar, but more advanced model in terms of dislocation movement. A plastic grain of length \( L \) in an elastic matrix is considered. The grain will relax until the stress reaches the yield value of the grain. When a stress is applied and continuously increased, an increasing number of dislocations form in a given area, and the stress is eventually balanced by the repulsive forces of the dislocations. Shear displacement of grains of length \( L \) can be approximated as:

\[ \frac{2L(\sigma - \theta)}{\mu} \]  \hspace{1cm} (2.3)

Jenkins [21] compared Cottrell’s model [22], in particular Equation (2.3), to experimentally derived stress-strain data. Figure 2.2 shows a plot of stress against strain for British Pile Grade A graphite, cyclically loaded and unloaded. Plotted on top of the data is the expected fitting curve derived from Cottrell’s model.
There is considerable agreement between the model and the experimental data. The data were subsequently used to calculate the $A'$ and $B'$ parameters in Equation (1.1):

$$A' = 0.0033 \text{ (ton/in}^2\text{)}^{-1}$$
$$B' = 0.0034 \text{ (ton/in}^2\text{)}^{-1}$$

These constants can be converted to more appropriate units:

$$A' = 0.046 \text{ (MPa)}^{-1}$$
$$B' = 0.047 \text{ (MPa)}^{-1}$$

This relationship was observed to be suitable up to stresses of around 0.6 ton/in$^2$ (8.36 MPa). Jenkins [21] suggested an explanation as to why his model became less accurate at high stresses. He proposed that the bulk modulus $E$ decreases at high stresses, as a result of an increased amount of localised cracking.

Since these early attempts by Jenkins [21] and Cottrell [22] to model stress-strain and deformation behaviour in nuclear grade graphite, our understanding of this behaviour has increased significantly. Modern models are often much more complex.
since they often take into account many of the physical processes that occur within an operational nuclear reactor. One such model by Tsang and Marsden [23] attempts to define the total strain acting upon the graphite in a nuclear reactor in terms of seven distinct components. The total strain $\varepsilon^{total}$ is defined using Equation (2.4):

$$\varepsilon^{total} = \varepsilon^e + \varepsilon^{pc} + \varepsilon^{sc} + \varepsilon^{dc} + \varepsilon^{th} + \varepsilon^{ith} + \varepsilon^{idc}$$

(2.4)

Where:

- $\varepsilon^e$ is the elastic strain.
- $\varepsilon^{pc}$ is the primary creep strain, and is recoverable.
- $\varepsilon^{sc}$ is the secondary creep strain, and is irreversible.
- $\varepsilon^{dc}$ is the dimensional change strain.
- $\varepsilon^{th}$ is the thermal strain.
- $\varepsilon^{ith}$ is the interaction thermal strain due to creep.
- $\varepsilon^{idc}$ is the interaction dimensional change strain due to creep, also a function of CTE.

Since the publication of this paper in 2006, there has been disagreement over whether the interaction dimensional change strain due to creep, $\varepsilon^{idc}$, should be included in the constitutive strain equation. The consensus now is that this term should no longer be included in Equation (2.4). The remaining six terms were quantitatively defined by Tsang and Marsden with the intention of using them as inputs for a stress analysis code to model irradiation-induced behaviour of graphite components in nuclear reactors.

Two main mechanisms [24, 25] are believed to underpin the stress-induced deformation response and eventual failure of irradiated graphite: microcracking and dislocation movement. Microcracks can combine if large enough in number, in size and if they are similarly aligned, resulting in the formation of large scale fracture paths and lowering the strength of the material, as discussed by Smith [26]. Large semi-stable dislocation densities can result in the build up of internal strains that can also cause the deformation or complete failure of the sample. The behaviour of dislocations shall be discussed in more detail in Section 2.1.3.
2.1.2 Porosity in Graphite

Graphite is a porous material, and the distribution, size and shape of pores are determined by a number of different factors such as raw materials, manufacturing process and ambient conditions the material is exposed to. As discussed by Fazluddin [24], pores typically form at the boundaries between crystallites and at sites of imperfect packing between binder and filler material.

The behaviour of pores can be described using the concept of poroelasticity, which describes the interaction between fluid flow and deformation of solids within a porous medium [27]. When external forces generate stresses in a porous medium, the volume of the pores and total porosity is affected. Fluid-filled pores will experience a change in pressure and the bulk material will deform plastically as a result of the fluid motion of the pores.

Attempts have been made to classify pores based on their lengths. Fazluddin [24] noted that three distinct pore lengths are typically considered during the study of nuclear graphite – micropores (<2nm), mesopores (2-50nm) and macropores (>50nm).

Pores can also be classified in groups based upon how they are formed and what their properties are. The most common categories of pore in graphite are:

- **Mrozowski cracks.** These are the smallest cracks typically present in graphite. As discussed by Sutton and Howard [28], these cracks are typically observed between the graphitic planes and are formed by anisotropic contraction of graphite as it cools after the graphitization phase of manufacturing. Mrozowski cracks have lengths typically ranging from 10 nm to 10 µm and widths from a few nanometres to 200 µm [29].

- **Gas evolution pores.** Studies by Li et al. [30] found that these pores are small, round, open and appear in the binder phase. They form during manufacturing when the green article is baked and gases are driven off, as discussed in Section 1.4.

- **Calcination cracks.** These elongated pores appear in coke, are elongated in size and are of the micro- to meso-scale [30]. They are formed during calcination stage, when the coke is heated to 1300°C [24].
It is accepted that an increase in porosity leads to a reduction in the strength of the material. However, there is disagreement regarding the physical parameters that underpin this relationship. Many different relationships have been proposed between the strength of a polycrystalline material \((S)\), its porosity \((\phi)\) and grain size \((d)\). Some of these relationships have been outlined by Knibbs [31]:

\[
\begin{align*}
\text{Hutcheon & Price:} & \quad S \propto \phi \omega^{-q} \quad (2.5) \\
\text{Knudsen:} & \quad S \propto e^{-m\phi} \quad (2.6) \\
\text{Orowan:} & \quad S = K_1 d^{-\frac{1}{2}} \quad (2.7) \\
\text{Petch:} & \quad S = K_1 + K_2 d^{-\frac{1}{2}} \quad (2.8)
\end{align*}
\]

where \(K, K_1, q\) and \(m\) are constants.

The proposed relationships differ between researchers, and porosity is not always considered to be a significant factor in the variation of the strength of graphite.

A study into the dependence of various material properties of graphite on porosity was performed by Hutcheon and Price [25]. The porosity was controlled by varying the number of impregnations and the binder fraction during the manufacturing process, as discussed in Section 1.4; and measurements of a range of material properties were made. The Young’s modulus varied linearly with porosity, while the strength decreased with increasing porosity by a power law of \(\varepsilon^{-1.6}\).

The studies into porosity-induced effects on material properties of graphite [24, 25, 26, 31] predict broadly similar behaviours, but tend to disagree on the smaller details. For example, the porosity-strength relations stated above in Equation (2.5) and Equation (2.6) both contain a negative power law term, but the exact value of the term varies. In a literature study in this field performed by Kelly [14], the author states that the existing studies represent the “tip of the iceberg”, and further developments of analytical techniques are required for more detailed study. Kelly [14] also noted that the difficulty of distinguishing between open and closed pores will also need to be overcome before porosity-induced effects can be fully understood.
2.1.3 Radiation-Induced Defects in Graphite

Graphite is subjected to large amounts of fast neutron irradiation in an operational nuclear reactor. More accurately, the atomic lattice is bombarded with energetic neutrons. As discussed in Section 1.1.1, fast neutrons of average energy 2 MeV [3] released by nuclear fission will damage the lattice structure and change the properties of the material.

Kelly [32] discussed the process in which defects in the atomic lattice are formed, as shown in Figure 2.3. Fast neutrons collide with carbon atoms and transfer energy to the lattice atoms. This energy transfer is greater than the binding energy that holds the atoms in the lattice, so the atoms are knocked out of it [32, 33]. These free atoms then collide with further lattice atoms, and a cascade begins. Studies have shown that one atom of every $10^8$ is displaced per second during the typical operation of an AGR.

![Figure 2.3: The formation of a displacement cascade induced by collisions of neutrons with the carbon lattice. Image courtesy of G. Hall.](image)

The free atoms typically move to more stable locations. Many atoms fall back to the lattice, filling the gaps left by other displaced atoms. However, as discussed by Thrower [33], there are two important structures that may form as a result of atoms not returning to the lattice planes:

- Some atoms may form semi-stable clusters between lattice layers, as shown in the left hand image in Figure 2.4. These are known as ‘interstitial loops’. They may grow by capturing further free carbon atoms or reach a stable size of 4±2 atoms [33].
• Linear groups of empty atom sites can build up and collapse parallel to the planes, producing a ‘vacancy loop’ as shown in the right hand image in Figure 2.4.

![Image](interstitial-vacancy-loops.png)

Figure 2.4: Interstitial and vacancy loops in the graphite lattice. Image adapted from Thrower [33].

Irradiation temperature has a significant effect on the formation of structures between lattice layers. An increased irradiation temperature will result in the formation of more interstitial loops, but will not affect the number of atoms in each individual loop [24, 33]. These interstitial and vacancy loops, collectively known as ‘dislocation loops’, and Thrower’s analysis of the effects of such features on the strength and deformation behaviour of bulk graphite, is well documented and corroborated by other studies [25].

Since the development of these models in the 1960s, advances in experimental techniques and the development of computer modelling have led to the formation of a number of alternate models of graphite deformation. Heggie et al. [34] have proposed the ‘buckle, ruck and tuck’ model, whereby damage is strongly dependent on temperature. Below a threshold of 250°C it is suggested that basal planes buckle, while above the threshold the layers fold over themselves.

2.1.4 Stress in Reactor Components

In a working reactor, a number of physical processes are present that can result in the build-up of stresses in reactor components. For example, stresses can grow as a result of temperature discontinuities between regions, or as a result of non-uniform neutron bombardment originating from irradiated materials [33]. If these stresses are
allowed to build up to high enough levels, it could result in physical damage to the graphite components.

In the AGR and Magnox reactor designs, the graphite moderating materials are machined into large bricks with channels running down their centres, into which fuel rods and control rods are inserted and coolant flows, as shown in Figure 2.5. Large arrays of these bricks are then connected together to form a graphite core.

![Figure 2.5: Image showing an Oldbury Magnox fuel rod being inserted into the channel running through the centre of a keyed graphite brick. Image courtesy of B. Marsden, University of Manchester.](image)

As discussed in Section 1.3, build-up of stresses in reactor components can result in cracking and the formation of large scale fracture paths. Figure 2.6 shows a composite image comprised of multiple photographs of an AGR graphite moderator. During reactor operation a fracture has opened along the entire length of the graphite brick.
If significant numbers of graphite components were to crack or deform as a result of the stresses that build up in working reactors, it is possible that the channels could become blocked. The inability to cool the reactor or control the rate of fission as a result of blocked fuel assembly channels, control rod channels or coolant channels would have significant safety implications. Hence it is important to understand how graphite responds to the build-up of internal stresses.

This issue is particularly important because graphite components in AGR and Magnox reactors cannot easily be repaired or replaced. Thus cracking or microstructural damage that occurs in the graphite moderator components has to be considered permanent. Over time the number and size of cracks will increase further, and will eventually become a major consideration when deciding of how long the
reactor can safely operate for. As cracking worsens, which is inevitable over time, the reactor becomes less safe, less efficient and more unpredictable in its operational behaviour. Therefore, it is unsurprising that there is demand for research into how graphite components respond to the stress-generation mechanisms that result in the cracking of bricks.

2.2 Studies into the Effects of Stress on Nuclear Grade Graphite

Despite the fact that graphite moderated reactors were embraced by relatively few countries around the world, there exists a considerable amount of research into its responses to stress. Two research groups in particular were noted for their contributions to the field: the Japanese Atomic Energy Research Institute and the University of Manchester.

The Japanese Atomic Energy Research Institute is noted for having conducted a series of experiments over many decades, focussing on variation of Young’s modulus in stressed graphite. Over this time an important experimental technique known as ‘time-of-flight’ measurements was used and optimised. These experiments are discussed in Section 2.2.1.

The University of Manchester is noted for a series of recent experiments into how graphite responds to stress, using a wide range of techniques. The timeliness of these experiments and the range of modern techniques utilised were useful for defining a novel research project to enhance our understanding of the behaviour of graphite. These experiments are discussed in Section 2.2.2.

Outside of these research groups, a series of research papers and projects were identified for being particularly insightful, important or novel to the field. The merits of these have also been discussed. These experiments are discussed in Sections 2.2.3, 2.2.4 and 2.3.
2.2.1 Studies by the Japanese Atomic Energy Research Institute

A number of studies have been conducted by members of the Japanese Atomic Energy Research Institute [36, 37, 38, 39, 40, 41] into the effects of stress on the Young’s modulus of graphite.

Yoda et al. [36] measured the Young’s modulus of 12mm x 12mm x 25mm stressed isotropic IG-11 graphite samples using a time-of-flight method. This process involved placing the sample between an ultrasonic transducer and a receiver, and determining the time taken for a pulse of known frequency to travel through the sample. If the density \( \rho \) of the sample is known, the Dynamic Young’s modulus \( E \) can be calculated using Equation (2.9):

\[
E = \rho V^2
\]  

(2.9)

where \( V \) is the velocity of the pulse.

It should be noted that \( \rho V^2 \) technically refers to the longitudinal modulus, or P-wave modulus, one of multiple elastic moduli that can be defined for homogeneous materials. However, the available literature into elastic modulus variation in nuclear grade graphite consistently refers to Equation (2.9), or similar forms of this equation, as a definition of young’s modulus.

An axial compressive load was applied to the sample to simulate the build-up of stresses. The main advantages of using axial loading for stress generation are that it is relatively simple and does not require the use of irradiated materials or high temperature environments; which would be necessary if the study was using the actual stress-generation processes experienced in an operational reactor. This technique for simulating reactor stresses was relatively new at the time, but has since become a well-established analogue for this purpose.

It was found that Young’s modulus decreases with increasing strain, as shown in Figure 2.7. The change in Young’s modulus was greater during tensile stress than compressive stress, and hysteresis loops were formed upon unloading and subsequent reloading. The explanation offered for the stress-induced changes in Young’s modulus was the deformation of filler particles and an increase in dislocation density. Grains in
graphite are believed to undergo plastic deformation when stress increases above a critical point, and only limited recovery is possible beyond this point when the stress is removed.

This experimental method has a number of limitations, as discussed by Marrow [42]:

- In order to ensure efficient sound energy transmission, there must be no gap between the transducer and the surface of the sample. Graphite can be very porous which can reduce the quality of the contact, even with the use of a suitable couplant. This may reduce the accuracy of time of flight studies on samples with uneven surfaces.
- Due to the size of the transducers, this technique is not suitable for small samples.
- The technique offers no information about sample homogeneity. A single value of dynamic Young’s modulus will be calculated, even if the material is comprised of multiple phases or exhibits complex morphology.
- Attenuation of the signal must be accounted for.

Another limitation of this study is the use of Equation (2.9) to calculate the Young’s modulus. Equation (2.9) calculates a simplified approximation of the actual value of Young’s modulus that fails to take into account a number of other important parameters that affect it. Many subsequent studies use more accurate equations for

Figure 2.7: Variation of Young’s modulus with compressive strain (left) and tensile strain (right). Hysteresis loops from repeated loading and unloading are visible in both cases [36].
determination of Young’s modulus from experimental data. For example, a more accurate equation that takes into account Poisson’s ratio ($v$), such as that used by Marrow [42] in his studies, would be better suited for this method, as shown in Equation (2.10).

$$E = \rho V^2 \frac{(1-2v)(1+v)}{(1-v)} \quad (2.10)$$

In 1973 Oku et al. [37] investigated the effects of pre-stressing graphite. Experiments were performed on Gilsocarbon, petroleum coke fine grained graphite (isotopic) and needle coke graphite (anisotropic), using the same time of flight setup as Yoda et al. [36]. Samples were axially prestressed using an Instron testing machine, and the level of applied stress on each sample was varied after the completion of each time of flight experiment. The Young’s modulus was found to linearly decrease as the level of pre-stress increased beyond an initial threshold pre-stress, as shown in the graph on the left in Figure 2.8. Oku concluded that the results supported the existence of a critical shear stress threshold which inhibits deformation at low stresses as proposed by Yoda et al. [36].

Figure 2.8: Left: Change in Young’s modulus for a number of nuclear graphites with increasing compressive pre-stress [37]. Right: Theoretical expressions from Walsh [43] fitted to the experimental data [37].
Oku et al. [37] proposed that these changes were explained by the formation and growth of cracks. Crack growth was modelled using theoretical expressions derived from a study by Walsh [43], and the equations generated fitted the data reasonably well. The modelled data are shown on the right hand graph in Figure 2.8. However, these modelling equations differ from the actual best fitting equations generated from the data, given by Equation (2.11):

\[
\frac{E}{E_0} = A\sigma_p^2 + B
\]  

(2.11)

where \(\sigma_p\) is the prestress and \(A\) and \(B\) are constants.

In 1977, Oku et al. [38] investigated Young’s modulus variation in isotropic Gilsocarbon graphite and anisotropic needle coke graphite using the time of flight method during the application of stresses. Both irradiated and unirradiated samples were studied. As shown previously [36], a decrease in Young’s modulus was observed with increasing compressive stress. It was proposed that the growth of cracks or an increase in dislocation density [36, 37], caused this change, which agrees with the hypotheses from previous studies by the group.

A subsequent experiment by Oku et al. [39] in 1998 utilised a similar time of flight method to calculate the Young’s modulus of pre-stressed graphite. The experimental process was the same as that of Yoda et al. [36], and Equation (2.9) was applied; neglecting to take into account Poisson’s ratio of the graphite. However, this experiment investigated changes at both room temperature and at 2283K. The stress-induced decrease in Young’s modulus at 2283K was much greater than that at room temperature, with \(\frac{E}{E_0} = 0.44\) for the former and \(\frac{E}{E_0} = 0.94\) for the latter. The authors were unable to confirm a proportional relationship between pre-stress and Young’s modulus because of the inability to conclusively prove that no other mechanism was causing the changes.

A study by Eto and Oku [40], investigated the effect of pre-stressing and thermal annealing on a variety of grades of graphite. The standard time of flight method was used, but a different equation was applied to calculate Young’s modulus:

\[
E = \left(\frac{q}{g}\right)V^2
\]  

(2.12)
\( \rho \) represents the apparent density of the material, the weight per unit volume; while \( g \) is the gravitational constant. Although this appears different to Equation (2.9) used by Yoda et al. [36], through conversion from apparent density to ‘traditional’ density the equations are analogous:

\[
E = \left( \frac{\rho}{g} \right) V^2 = \left( \frac{W}{gV'} \right) V^2 = \left( \frac{mg}{gV'} \right) V^2 = \rho V^2
\]  

(2.13)

where \( W \) is the weight and \( V' \) is the volume of the sample.

The measurement technique adopted by Eto and Oku [40] is attributed to Sato and Miyazono [41], who performed time-of-flight measurements of elastic moduli in graphite. Their calculations of elastic moduli utilised Equation (2.14):

\[
E = \frac{\gamma l^2}{gt^2} = \frac{\gamma}{g} V^2
\]  

(2.14)

where \( \gamma \) is the specific weight of the sample, equal to the product of density and the gravitational constant. Hence:

\[
E = \frac{\rho g}{g} V^2 = \rho V^2
\]  

(2.15)

As well as confirming the earlier observations of Young’s modulus variation, Eto and Oku [40] performed annealing experiments to determine whether irradiation induced changes in Young’s modulus could be reversed. The study concluded that the moduli of extruded graphite can almost fully recover when annealed up to 1000°C, while only partial recovery of moulded graphite are possible by 2000°C.

The last paper in the group, the aforementioned study by Sato and Miyazono [41], used time of flight studies to propose an explanation of how irradiation can change the Young’s modulus of graphite. As discussed in Section 2.1.3, irradiation by neutrons displaces carbon atoms, forming vacancies in the lattice planes and interstitials between the planes. These interstitial clusters cause an increase in internal strains and make the nearby lattice layers more resistant to further displacement. This
increases the elastic modulus of the material. However, Sato and Miyazono propose that this effect is counterbalanced by the increasing numbers of vacancies reducing the elastic modulus. The latter mechanism becomes increasingly dominant at higher irradiation doses, diminishing the rate of change of elastic moduli and eventually holding it steady.

All of the above experiments conducted by scientists at the Japanese Atomic Energy Research Institute share a number of common characteristics. The time-of-flight method is used in each case. Variations of the same formula are used to determine Young’s modulus, resulting in inconsistencies in the accuracy of the results of each study. Each experiment also used large graphite samples, with diameters ranging from 5 to 80 mm and lengths typically around 10 mm. Despite the differences in methodologies, the findings of each study are largely consistent, with an increase in applied stress causing a reduction in Young’s modulus and vice versa. The growth of cracks is cited as the most plausible explanation for these observations, while there is evidence of an increased density of dislocations between the lattice layers.

The experimental methodology and analytical techniques used by the group have not changed significantly throughout many decades of study. Given that no significant increase in data quality has been observed, it may be that different experimental methods are required to further our understanding of the behaviour of graphite. Even considering more recent time of flight studies both inside and outside the field of graphite [44, 45, 46], it appears that alternate experimental methods may be more insightful than further experiments using the well established time of flight technique.

However, despite the few methodological flaws with the time of flight approach and the inconsistencies with methods for Young’s modulus calculation, the studies by the Japanese Atomic Energy Research Institute have yielded useful data regarding the behaviour of Young’s modulus in stressed graphite and its contribution to the field should not be underestimated.
2.2.2 Studies by the University of Manchester

The Nuclear Graphite Research Group at the University of Manchester is one of the few groups in the United Kingdom dedicated to the study of nuclear graphite. Researchers in this group have published a number of papers [47, 48, 49] investigating variation of material properties of stressed graphite. Of particular interest are two recently completed postgraduate research projects by Bakenne [45] and Bodel [46] that focus on the variation of the material properties of graphite when subjected to stress.

2.2.2.1 Study by Bakenne (2012)

Bakenne [45] investigated the deformation and modulus changes in stressed graphite. PGA and GilsoCarbon were hydrostatically stressed to 200MPa and axial and circumferential strain measurements were made using strain gauges. Dynamic Young’s moduli were measured through the ultrasonic time of flight method, and the pore structure of graphite was investigated, both before and after loading. A number of existing models of the microstructure of graphite were studied with the aim of explaining the observed properties. Many of the methods of Young’s modulus calculation are reminiscent of the studies conducted by the Japanese Atomic Energy Research Institute.

A number of experiments into variation of Young’s modulus and porosity were performed. Some experiments involved the in-situ application of load, while other experiments were limited to observations before and after load application. Since the residual stresses that exist after loading has been removed are known to be small compared to the stresses generated during loading, the lack of in-situ data is a major limitation to the usefulness of these data. Bakenne plotted the Young’s modulus and porosity for each sample as shown in Figure 2.9.
Bakenne observed a “vague downward trend” of Young’s modulus with increasing porosity for PGA in the range studied, as shown in Figure 2.9; while Young’s modulus in Gilsocarbon was found to be independent of porosity. The results for PGA appear to agree with most of the existing literature [50, 51, 52], however the usefulness of this data is limited due to the small amount of data and its very limited range. In addition, the observed porosity-independence of Young’s modulus in Gilsocarbon warrants further investigation. It is unclear why the porosities in the PGA-WG and PGA-AG samples are so different, since they were cut from the same PGA graphite brick. The only difference between the two samples is the orientation with respect to the direction of the ultrasonic pulse, so there should be no reason for the PGA-AG sample to exhibit greater porosity than the PGA-WG sample. The lack of error analysis and appropriate error bars in Figure 2.9 also limit the usefulness of this study.

Young’s modulus and open pore volumes were studied in samples before and after loading to further investigate the above results. After initial measurements of the material properties were made, the samples were hydrostatically compressed and were subsequently unloaded. Figure 2.10 shows the relationship between dynamic Young’s modulus and shear modulus\(^2\) with porosity for PGA graphite.

\(^2\)The shear modulus is the ratio of shear stress to shear strain, and is a measure of a material’s resistance to shearing strains.
In common with other studies [46, 50], open pore volume and Young’s modulus were observed to decrease after loading. The downward trend of Young’s modulus with increasing porosity is still present after loading with the sample compressed parallel to the extrusion direction, while the trend is less clear for the sample compressed perpendicular to the extrusion direction.

![Figure 2.10: DYM and shear modulus in PGA graphite plotted against open pore volume (OPV) before and after loading. Top: Measurements with the grain. Bottom: Measurements against the grain [45].](image)

Following these initial experiments, ultrasonic time of flight measurements were used to investigate Young’s modulus variation. Young’s moduli were calculated using longitudinal and transverse wave velocity measurements. This experimental
method, along with the equations used to interpret the data, were derived from a study by Asmani et al. [52], discussed in Section 2.3.

However, it appears that an incorrect equation was used to calculate Young’s modulus from longitudinal and shear wave velocities (Eq. 3.19, p. 55). Without access to the raw data it is not possible to confirm whether an invalid equation has been used for the Young’s modulus calculation, or whether this is just a publishing error. If an incorrect equation has been used, these results, and any conclusions derived from them, should be disregarded, and caution should be exercised when analysing any further data from Bakenne.

Bakenne’s investigations into Young’s modulus variation were entirely focussed on the bulk material, and were carried out using time-of-flight studies. As such, the experiments have much in common with previous studies by the Japanese Atomic Energy Research Institute. There is also agreement in the results and overall trends observed.

One of the main limitations of Bakenne’s research into stress-induced deformation of graphite is that much of the data is restricted to before and after loading measurements. No in-situ data during loading is available for the porosity studies. Since much of his other research, such as that into Young’s modulus variation, was conducted during loading, the lack of in-situ porosity data represents a missed opportunity that may have yielded valuable data.

### 2.2.2.2 Study by Bodel (2012)

The second important study recently completed at the University of Manchester was that by Bodel [46]. Bodel performed a series of investigations into the relationship between the microstructure of graphite and its Young’s modulus. Dynamic and static tests were performed using three distinct techniques – time of flight, impact excitation and four point bend testing – to study how Young’s modulus changes when stressed. Static testing techniques are isothermal, while dynamic tests are adiabatic, and values of static and dynamic Young’s modulus differ slightly. Equation (2.16) below shows an equation that connects static and dynamic Young’s modulus values, $E_s$ and $E_d$, respectively.
In studies of nuclear grade graphites, static moduli are typically calculated through deformation studies of materials during the application of a force, while dynamic moduli are typically calculated through studies of ultrasonic wave propagation through the material, as discussed in Section 2.1.1.

The first investigation into Young’s modulus was performed using the time of flight approach discussed extensively in this review. This is a dynamic technique, hence values of dynamic Young’s modulus were calculated. Equation (2.10) [42] was used to determine values of Young’s modulus from the longitudinal pulse velocity, with the effects of Poisson’s ratio taken into account. Figure 2.11 shows the calculated Young’s moduli for four different grades of graphite, plotted against the density of the material.

Comparing these data to results in a similar study by Brocklehurst and Kelly [17], Bodel noted agreement with data for PGA, while results for Gilsocarbon were higher than expected. The latter was explained by the use of a block of greater density than that used by Brocklehurst and Kelly.

\[
E_D = E_S + \frac{E_S^2}{9C_p} \left( \frac{\partial^2 V}{\partial T^2} \right)_p T \quad (2.16)
\]

![Figure 2.11: Dynamic Young's modulus plotted against density for four grades of graphite, including data with and against the grain for anisotropic PGA (PGA WG and PGA AG respectively), determined using time of flight methods [46].](image-url)
The merits and limitations of the time of flight technique have already been discussed in detail. Bodel used the most accurate equation for this study, Equation (2.10), taking Poisson’s ratio into account. Bodel also attempted to minimise experimental difficulties such as those caused by transducer orientation and imperfect contact between transducers and the sample [42]. The methodology employed is among the most rigorous of all time of flight experiments studied, and the results have been treated accordingly.

The second measurement technique employed by Bodel is impact excitation, a method of determining the Young’s modulus through study of resonant frequencies of the material. This is also a dynamic technique. For this experiment the samples must be machined into geometries capable of resonating when impacted, such as a long, thin beam. Using an experimental methodology defined by Roebben et al. [53], the Young’s modulus was determined by calculating the fundamental flexural frequency. For a sample of mass $m$, length $L$, width $W'$ and height $H$, the Young’s modulus is given by Equation (2.17):

$$E = 0.9465 \left( \frac{m f_f^2}{W'} \right) \left( \frac{L^3}{H^3} \right) k_1$$

(2.17)

Where $f_f$ is the fundamental flexural frequency and $k_1$ is a correction factor accommodating Poisson’s ratio and beam dimensions. It must be noted that this method is only suitable for the study of isotropic materials, and any data collected for anisotropic materials will be of questionable quality [53]. Figure 2.12 shows data for the Young’s modulus of various isotropic grades of graphite with respect to material density, similar to the data presented in Figure 2.11.
The above data agrees with the data from time of flight experiments. Bodel noted the difficulty in machining the polycrystalline graphite samples to suitable dimensions for this study, particularly for oxidised samples; and deemed it experimentally unviable to machine the limited amounts of irradiated material available into numerous long, thin beams. For this reason, and the difficulty of studying anisotropic graphite, the impact excitation method was deemed to be experimentally less practical in this case compared to the time of flight method.

The final method, four point bend testing, provided data on the stress-strain response and values of various moduli for the sample being tested [54]. This method differs from the other methods discussed above in that it is a static technique, hence it determines the static Young’s modulus as opposed to the dynamic Young’s modulus. An experimental arrangement similar to Figure 2.13 was used to determine the Young’s modulus variation as long, thin graphite rods were stressed. The force was applied by two loading spans, each providing half of the total force.
Table 2.1 compares values of static and dynamic Young’s moduli derived from four point bend testing, impact excitation and time of flight experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_s$ [GPa]</th>
<th>$E_d$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D 1.1</td>
<td>-</td>
<td>12.2</td>
</tr>
<tr>
<td>D 1.2</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>D 1.3</td>
<td>10.3</td>
<td>12.2</td>
</tr>
<tr>
<td>D 1.4</td>
<td>11.0</td>
<td>12.5</td>
</tr>
<tr>
<td>D 1.5</td>
<td>10.8</td>
<td>12.0</td>
</tr>
<tr>
<td>D 1.6</td>
<td>10.7</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison between static ($E_s$) and dynamic ($E_d$) Young’s moduli for six samples using the three experimental methods discussed above [46].

There is strong correlation between the dynamic Young’s modulus data from the time of flight and impact excitation techniques, but the time of flight data predicts consistently slightly greater modulus values. Bodel noted that values for all samples range by around 5% for the dynamic measurements and 7.5% for the static measurements, and that the static modulus values are typically 10-15% lower than the dynamic values.

The second part of Bodel’s research involved investigating how stress affected the Young’s modulus of various grades of graphite. As with the majority of research
conducted by other groups, the investigations were performed using large samples, with typical edge lengths in the order of centimetres.

The samples were axially compressed using a compression rig. Pulse transmission velocities were calculated for a range of graphite samples, both parallel and perpendicular to the grain where applicable, and were plotted against the applied compressive stress. Figure 2.14 shows a typical plot of pulse velocity against compressive stress.

![Graph showing pulse velocity against compressive stress](image)

Figure 2.14: Variation in transmission velocity with applied load. The sample is PGA compressed perpendicular to the grain, and the longitudinal pulse is being measured. Repeated loading and unloading were performed on the sample [46].

Data was collected and presented in this format for multiple types of graphite, irradiated and unirradiated; and in directions with and against the grain direction. From these graphs various material parameters related to the structure and stress response of graphite were calculated. An excerpt of these results is shown in Table 2.2.

Bodel noted that these results correlate well with previous studies by Brocklehurst and Kelly [17], shown in Table 1.4, and that the static results were typically 20% lower than the dynamic results across all grades of graphite tested.
The final part of Bodel’s project was an in-situ study of how stress affects the microstructure of graphite. Imaging experiments were performed using a confocal laser scanning microscope, capable of obtaining high resolution images of the surface of a material, with the aim of observing microstructural deformation and crack propagation in axially stressed graphite. This study was entirely qualitative, with images such as those in Figure 2.15 showing the closure of microcracks as a graphite sample was compressed by a compression rig.

While the images from this study do show evidence of crack growth and propagation, the usefulness of these two dimensional images is limited. For example, it is not always possible to differentiate between changes in the pore structure and bending of the sample during compression simply by looking at two dimensional images. A method of analysing images with a degree of depth selectivity would resolve this issue. Also, a method of studying the interior of the material, in particular the study of interior pores would be more useful than just observing the surface profile.

The other main limitation of the analysis of the confocal microscopy data is that it was purely qualitative, based upon a visual study of the images by eye. No attempt was made to quantify any of the behaviours that were being observed. Given the significant amount of high resolution data available, the lack of a quantitative analysis is unfortunate as it would have most likely yielded novel insight into the behaviour of graphite.
From his study, Bodel made a number of conclusions about the changes in Young's modulus due to stress. In Gilsocarbon, the reduction in pulse transmission velocity with increasing compressive stress, and hence the reduction in dynamic Young's modulus, was attributed to the opening of cracks during loading. The transmission velocity recovered when the load was reduced and eventually removed, implying that the cracks were closing. Gilsocarbon and PGA compressed with the grain exhibited similar behaviour as long as the load applied to the PGA did not exceed 20% of the failure load – above this value no recovery was observed.

For PGA compressed against the grain, behaviour was similar for loads below 20% of the failure load. However, the more the load exceeded this figure, the greater

Figure 2.15: Micrographs of the surface of graphite as a PGA sample is axially loaded, produced using a confocal laser scanning microscope. Image adapted from Bodel [46]. Significant deformation is observed in the elliptical filler particle near the centre of the image.
the induced reduction in transmission velocity after unloading. Subsequent reloading caused the transmission velocity to recover to its initial value. Interestingly, this velocity-strain relationship is the opposite of that exhibited for Gilsocarbon and for PGA compressed with the grain. This was attributed to the filler particles receiving most of the damage and crushing during loading, while when PGA is compressed with the grain, filler particles become stiffer and more resistant to damage.

Overall, Bodel’s research has much in common with that conducted by Bakenne [45] and the Japanese Atomic Energy Research Institute [36, 37, 38, 39], among others. The use of large samples and the time of flight method are both well established, and appear to have been optimised in this project. In general, the data agrees with other relevant studies, and the conclusions made by Bodel are in line with what would be expected. The lack of quantitative analysis of the confocal microscopy data is the only major limitation to Bodel’s research.

2.2.3 Other Studies of the Effects of Stress on the Properties of Graphite

While the Japanese Atomic Energy Research Institute and the University of Manchester represent the main bodies of literature studied, there are a number of papers from other institutions that document relevant research and yield useful information.

Fang et al. [55] attempted to create a model of stress build-up within a graphite block when exposed to the conditions of a working nuclear reactor. This study differentiates itself from the numerous existing modelling studies by focussing on the use of graphite moderators in High Temperature Reactors (HTRs), and hence the graphite geometries being studied are specifically for HTRs. Equation (2.4) [23] is used to provide the fundamental inputs, with the exception of the interaction dimensional change strain term (as discussed in Section 2.1.1), and the merits of a number of different models of irradiation creep are discussed.

The study itself considers a sample of extruded H-451 graphite machined to geometry suitable for use as a reflector block in an HTR, as shown in Figure 2.16. Two points on the block, labelled A and B in Figure 2.16, were selected for study – one at the outer edge of the brick (B) and one at the edge of a fuel and coolant channel (A).
Since the geometry, irradiation and temperature are significantly different at each location, the build-up of stresses is expected to behave differently.

Figure 2.16: Stress distribution in a block of H-451 graphite at the end of its operational lifetime. Points A and B are defined for further study. Unit: Pa [55].

For the two locations marked in Figure 2.16, the theoretical stress history for a component in a nuclear reactor was calculated based upon the models derived from Equation (2.4). These results were plotted over the lifetime of the brick as shown in Figure 2.17.

Figure 2.17: Variation of internal stress build-up with time in an H-451 graphite component measured at the two locations defined in Figure 2.16 [55].
As anticipated, the stress build-up behaviour is significantly different at each of the two locations. For point A (at the outer edge of the fuel channel), very little stress built up until a time threshold point was reached, after which a quadratic rate of change was observed. By comparison, at point B (at the outer edge of the component) stresses began to build up immediately, peaking after around 18 years of operation. After this point, the stresses began to relieve themselves at a similar rate to which they built up.

Fang’s paper provides a useful comparison of some of the different models of stress build-up in graphite. It also emphasises the importance of putting experiments and research into physical context. The majority of physical experiments discussed so far use sample sizes and geometries that are not necessarily comparable to the way graphite is used in nuclear reactors. This is often due to the limitations of the experimental apparatus or methodology. Although similar processes are occurring at points A and B in Figure 2.16, the stress behaviour is very different due to the locations of the points with respect to material structures and boundaries.

By comparison, models and simulations can be created for sample geometries that are directly representative of the components that are used in nuclear reactors, instead of requiring the use of small samples that may not be representative of full graphite bricks. This represents one of the major advantages of modelling experiments over physical experiments, and is a reminder that physical experimental data must be viewed in the context of a working reactor for it to be useful.

Preston and Marsden [47] have studied the changes of the coefficient of thermal expansion (CTE) in Gilsocarbon, when subjected to tensile and compressive static loading. Compressive loads were found to increase the CTE parallel to the loading direction, and tensile loads were found to decrease it. The opposite was true perpendicular to the loading direction – compressive loading reduced the CTE while tensile loading increased it. An interesting mechanism is proposed to account for these changes. Preston and Marsden proposed that the stress-induced changes in CTE may be due to the change in orientation of the crystallites. This mechanism had been previously discussed by Sutton and Howard [28] for changes in the material properties of anisotropic graphite such as PGA. However this explanation has not yet been confirmed.
The hypothesis of crystallite reorientation in graphite when exposed to stress, if valid, will also affect the Young’s modulus - particularly with respect to anisotropic graphite. There is currently not enough experimental evidence to confirm this hypothesis. Reorientation of crystallites may be a viable explanation for the observed changes, and further investigation is required.

A subsequent experiment by Marsden et al. [48] investigated the changes in material properties in irradiated Gilsocarbon, heated between 650 and 750°C. The Young’s modulus was found to rise with increasing radiation dose, as shown in Figure 2.18. An increase was observed up to a dose of $20 \times 10^{20} \text{n/cm}^2$, followed by a plateau; whilst a subsequent increase in the Young’s modulus occurred between doses of 50 and $75 \times 10^{20} \text{n/cm}^2$. The initial increase in Young’s modulus was attributed to pinning of dislocations in the basal plane.

There is disagreement on the cause of the second increase. Marsden et al. comment that existing studies attribute this behaviour to a build up of internal stresses. However, a finite element modelling study by Hall et al. [49] suggested it is caused by closure of Mrozowski cracks and accommodation porosity, a type of thin lenticular crack [28]. Further experimental study is required to conclusively confirm the process that underpins the second dose-induced increase in Young’s modulus.

![Figure 2.18: Change in Young’s modulus with fast neutron dose. $E_0$ represents the unirradiated Young’s modulus, while $E_{x,y,z}$ represent moduli measured in the x-, y- and z-directions respectively [48].](image)
2.2.4 Studies into the Pore Structure of Graphite

Kane et al. [56] performed a series of imaging experiments using an optical microscope to investigate the microstructure and pore structure of various nuclear grades of graphite. Properties including pore area, pore eccentricity and total porosity were quantified through study of a series of images of the surfaces of graphite samples.

Calculations of open pore eccentricity, \( e \), at the surface of the samples were performed by using a computer programme to fit ellipses to pores and determining eccentricity values from the minor and major axis lengths, \( m \) and \( M \) respectively, of the ellipses. These data were used in conjunction with Equation (2.18) to calculate values of pore eccentricity:

\[
e = \frac{\sqrt{M^2 - m^2}}{M}
\]  

(2.18)

Eccentricity values can range from zero to one. An eccentricity value of zero is indicative of a perfect circle, while a value of one represents a straight line.

Figure 2.19 shows the probability distribution function of pore eccentricities. The resolution of the images enabled pores as small as approximately 15 \( \mu m^2 \) to be studied.

![Nuclear Graphite Pore Shape Distributions](image)

Figure 2.19: Probability distribution function of pore shapes defined by ellipses. The second derivative of the intensity function in the range \( 0.95 < e < 1 \) is inset [56].
The use of this equation relies on the assumption that pores are all shaped like ellipses. Through qualitative study of existing data, this assumption becomes progressively less accurate as pore size increases. Many of the smallest pores are simple enough to be well defined by an ellipse, but the complexity of pore shape increases with size meaning that this analysis cannot accurately define many of the larger pore structures. This reduces the accuracy of the data presented in Figure 2.19, and limits the usefulness of any conclusions derived from it.

However, the study does disprove the original hypothesis proposed by Kane et al. that pores in the filler and binder phases would behave differently, thus exhibiting a bimodal eccentricity distribution, since the pore types would have distinct shapes. Instead, a continuous distribution was observed, with no clear transition or distinction between pore types.

2.3 Studies into the Relationship between Porosity and Young’s Modulus

Many of the studies discussed so far either focus on the variation of Young’s modulus due to stresses within the graphite or the variation of the pore structure due to stresses. It is important to consider that these two processes do not occur independently of one another, and a number of studies have been performed to investigate the relationship between the Young’s modulus and the porosity of various grades of graphite.

As discussed by Wagner et al. [50], the effects of pore morphology on the material properties of graphite are poorly understood. The main reason for this is the difficulty of determining unambiguously which changes are due to the porosity alone – a difficulty that is still experienced in current research. To circumvent this difficulty, Wagner et al. attempted to create a series of graphite samples which only differed by the fractional porosity. This meant that inter-planar spacing, crystallite thickness, orientation, and other properties relating to the structure of the matrix remained constant across each sample.

Wagner et al. investigated thermal and physical properties of a number of different grades of graphite. For each grade of graphite, a series of samples were
manufactured to be identical, except for their fractional porosity. A thin rod resonance method, whereby the sample’s resonant frequency was determined by a capacitance probe technique [57], was used to determine the Young’s modulus of each sample. The limitations of this technique have already been discussed in Section 2.2.2.2 in the context of Bodel’s research [46].

An inverse linear relationship was observed between porosity and Young’s modulus in the range of porosities studied, as shown in Figure 2.20.

![Figure 2.20: Effect of porosity on elastic properties of graphite [50].](image)

However, the accuracy of these results is questionable, since the data indicates that extrapolated values of elastic moduli are too low by a factor of 3 compared to previous studies [8, 58]. Another flaw is seen in the thermal resistivity data: when extrapolated to a single crystal density of 2.25 g/cm³, the value is a physically impossible negative value.

These invalid results and physical inconsistencies with existing data suggest that the behavioural models for these graphite samples are flawed. The authors attempt to explain these problems by proposing that porosity is split into two distinct types – bulk porosity and filler porosity. The former is thought to arise from shrinkage and gas evolution during manufacturing, while the latter occurs due to stress-induced basal plane delaminations. Each classification of porosity is proposed to have a different effect on the material properties of graphite, with the authors acknowledging the need for further study into this hypothesis.
Asmani et al. [52] performed an investigation into the effects of porosity on Young’s modulus in alumina ceramics. The fundamental experimental method was similar to the traditional time of flight approach; however a pulse echo method that measured the velocities of the pulse and its reflection was used, hence only requiring a single transducer. Also, a different equation was proposed to convert from wave velocity to Young’s modulus. An equation in terms of longitudinal and transverse velocities, $V_L$ and $V_T$ respectively, was used to derive values of Young’s modulus, as shown in Equation (2.19):

$$E = \rho V_T^2 \left( \frac{4V_T^2 - 3V_L^2}{V_T^2 - V_L^2} \right)$$  \hspace{1cm} (2.19)

Although this equation was derived for the analysis of alumina ceramics, it is applicable to any porous isotropic solid, such as Gilsocarbon. This equation was used by Bodel [46] and by Bakenne [45] (the latter unsuccessfully) to calculate Young’s moduli in stressed Gilsocarbon.

However, a difficulty arises when using this equation when studying anisotropic materials. When measuring the transverse velocity, $V_T$, the orientation of the transducers must be considered. Different orientations relative to the grain direction will result in different transverse velocities being recorded, as shown in Figure 2.21, with Bodel [46] observing velocity variation of up to 25% in studies of PGA at different transducer orientations. There is disagreement over the optimal transducer alignment, but a common solution is to take an average of the velocity values with the transducer orthogonal to the grain, i.e. images B and C in Figure 2.21 [46].
Kováčik [51] investigated the correlation between Young’s modulus and porosity in highly porous materials. This relationship was studied using percolation theory [60], a model of the clustering and spread of random components in a medium. Percolation theory is particularly useful for the study of porous materials, since the pores typically act as quasi-random connected clusters. It has been adopted for use in a number of studies into the behaviour of graphite, such as the study of CTE variation by Hacker et al. [61].

Through experimental study of a variety of porous materials, Kováčik [51] proposed that the behaviour of Young’s modulus, as analysed with percolation theory, is identical to a relationship derived by Phani and Niyogi [59] to predict elastic properties of porous media:

$$E = E_0 (1 - \frac{\omega}{\omega_c})^{f'} \quad (2.20)$$

where $E$ represents the effective Young’s modulus, $E_0$ is the Young’s modulus of the solid material, $\omega$ and $\omega_c$ are the porosity and critical porosity (where $E = 0$) respectively, and $f'$ is a parameter dependent on pore geometry.

The above equation, alongside Kováčik’s studies, shows an inverse linear relationship within the studied range between local Young’s modulus and porosity in
porous media. Preparation method, powder size and powder shape have been shown to influence the rate of change of Young’s modulus with varying porosity. For example, a greater pore size was seen to increase the dependence of Young’s modulus on porosity.

These methods can be applied to the research of graphite, since graphite is a porous material. It would be interesting to see how the relationship between Young’s modulus and porosity defined in Equation (2.20) compares to those proposed by Asmani et al. [52] and the Japanese Atomic Energy Research Institute.

2.4 Conclusions and the Proposed Experimental Program

There is a considerable amount of research into the effects of stress on the material properties of graphite. The research discussed in this chapter represents the extent of our current understanding into how graphite responds to stresses. From this research, insight has been gained into experimental methods and analytical techniques that are popular and those that are unpopular; those that are successful and those that are unsuccessful. The main conclusions from this literature study are presented below.

2.4.1 Conclusions

Most Young’s modulus studies on nuclear grade graphite were carried out using the time of flight method, discussed in Section 2.2. Although this methodology has remained popular for many decades, there remain flaws associated with the methodology and, as discussed in Section 2.2.1, disagreement over how the data should be analysed. In addition, due to the considerable amount of existing research using this technique and the consistency of the determined parameter relationships across different research groups and over many decades of study, it appears that this method has reached the point where it provides little new information regarding the material properties of graphite. A novel, more detailed methodology is desirable.

Researchers have attempted to create models or derive equations to explain the observed stress-induced changes. Numerous models of the behaviour of graphite exist, each with their own merits, flaws and limitations, depending on which
circumstances they are applied to. The models vary significantly in complexity and in the explanations of the behaviour they predict. However this predicted behaviour is often very similar. For example, Jenkins’ [21] relatively simple block and spring model predicts similar behaviour in graphite as the complex percolation theory proposed by Kováčik [51] and Phani and Niyogi [59]. It is difficult to determine whose models are the best approximation of the behaviour of graphite without further physical study of the material.

The common denominator of the majority of research studied is the focus on the bulk material. The effects of stress on Young’s modulus and porosity in bulk graphite are well understood, while the mechanistic understanding at the microscale is not investigated. The likely reasons for this are that existing, well established experimental methodologies (such as the ultrasonic time of flight method) are unsuitable for microscale measurements, and that using other techniques to make these measurements at the microscale is significantly more complex than at the bulk level. This represents a significant gap in the existing research; one that could yield valuable information to sit alongside the well-researched bulk scale. Given that the behaviour of bulk graphite is predominantly underpinned by changes to the material at the microlevel, any studies that aim to explain the observed changes using data at the bulk scale will be of limited use.

However, there are also difficulties associated with studying material behaviour at the microlevel. Many techniques that are used to acquire data at this level, such as high resolution imaging and X-ray diffraction studies, require the use of small samples. These samples typically exhibit dimensions that are orders of magnitude smaller than the graphite bricks used in nuclear reactors. There is a risk that such small samples may not be representative of the actual graphite components. In addition, the small samples may not be able to withstand the physical conditions that exist in an operational nuclear reactor, so alternate methods of simulating these conditions may be required for stress-induced behaviour studies.

There have been previous attempts to model these material properties at the microscale, such as those by Hall et al. [49]. However, while such theoretical models enable prediction of material properties and allow planned responses to specific physical conditions, they are significantly enhanced with real data to support the theories or act as inputs. A series of physical experiments studying the microscale
effects of stress will yield a clearer and decisive understanding of the behaviour of
graphite at this level.

In order to gain an increased understanding of how stresses affect graphite, it
was decided to focus upon behaviour at the microlevel. At the microlevel the porosity
can also be studied in great detail, which is useful since the pore structure is known to
play an important role in determining the strength and structural integrity of graphite
components. Therefore, an experiment to investigate the effects of stress on the
Young’s modulus and pore structure in graphite is proposed.

2.4.2 Experimental Proposal

In order to study the pore structure of graphite, a method of imaging the
interior of the samples to produce a three-dimensional representation of the object is
required. The most suitable method of achieving this is using X-ray computed
tomography (XCT). X-ray computed tomography is a widely used method of imaging
the interior of materials in three-dimensions, and studies [22, 45, 46, 56, 62] have
shown that X-ray tomography is particularly well suited for the microscale imaging of
porous solids such as graphite. Tomography can produce detailed three-dimensional
images of graphite, with achievable resolutions depending on the tomographic
scanning equipment available and the size of the samples being studied. It is common
for such studies to allow resolution of the order of a few microns. Sample sizes for high
resolution tomographic imaging must be of the order of millimetres, resulting in the
difficulty of determining whether the observed behaviour is truly representative of the
bulk material.

Confocal laser microscopy (CLM), as performed by Bodel [46], can be used to
produce a surface profile of a material. Commonly referred to as a ‘quasi-3D’ or ‘2.5D’
technique, confocal laser microscopy can acquire images with a degree of depth
selectivity, which is particularly useful for highly porous materials such as graphite.
Despite not observing the full interior structure, confocal microscopy can still provide
useful information on the stress induced effects on the microstructure of graphite –
albeit with limited depth sensitivity. As discussed in Section 2.2.2.2, Bodel’s study
utilised confocal microscopy images, but was purely qualitative and limited to two
dimensions. A three dimensional, quantitative study would allow the acquisition of much more useful data for a stress-induced behaviour study.

Even though sub-3D techniques are objectively inferior to 3D techniques when attempting to study processes that occur in three dimensions, such as stress-induced deformation of graphite reactor components, techniques have been developed to enhance the usefulness and relevance of sub-3D studies. Stereology is a technique that enables three-dimensional information to be acquired from two-dimensional data. The technique uses random sampling in conjunction with two-dimensional data, for example the cross-sectional area of a feature, to estimate three-dimensional parameters, such as the volume of the feature.

In order to investigate how porosity is affected by stress, the samples must be subjected to varying degrees of stress without disrupting the image scanning process. It has been shown that applying an axial load can be used to represent the build-up of reactor stresses in graphite [36, 38, 39, 45, 46]. The technique is relatively simple, well understood and reliable. Most importantly, bespoke compression rigs that are compatible with the tomography and confocal microscopy apparatus are available for use, such as that designed by Kareh et al. [62]. Therefore, this technique shall be used to generate stresses in the samples during imaging.

Each sample will be axially compressed to a range of loads and tomographic and microscopic scans will be performed. Images of each sample acquired during the application of progressively greater loads will allow observations of changes to the pore structure to be made. Using appropriate image analysis software, these behaviours can be quantified.

A third experimental technique that can be used to study stress-induced damage growth is X-ray diffraction (XRD). X-ray diffraction is used to quantify properties of the atomic structure of graphite by studying the diffraction behaviour of X-rays as they are projected upon a sample. Since stresses in graphite are known to damage the repeating lattice structure of the material [32, 33], performing XRD on stressed graphite samples will provide a quantitative analysis of damage to the atomic structure of the material.

Other techniques were considered for use in the project but were ultimately rejected. Scanning electron microscopy is a technique that uses a beam of electrons to produce images of materials at resolutions down to approximately 1 nm. This
technique was rejected since the project was focussing on the millimetre to micrometre lengths scales, and using a scanning electron microscope would be excessive for this purpose. Polarised light microscopy techniques utilise polarised light to enhance the contrast in images and allow the observation of three-dimensional structures. Polarised light microscopy was not used due to a lack of understanding of the technique, however future experiments in this field may utilise this technique.

This experimental program will yield valuable information regarding how material properties of graphite are affected by stress at the microscale; and will provide insight into the conditions to which graphite is subjected within the environs of a working nuclear reactor. Each aspect of the project is designed to be novel in the field of nuclear graphite study or to represent a significant improvement or advance over previous studies. Therefore, the results are expected to provide a novel contribution to the current knowledge base of nuclear graphite study.

2.5 Summary

- The existing literature was studied to determine the current understanding of stress-induced deformation behaviour of graphite, and a novel experimental programme was proposed.
- Fundamental stress-strain behaviour of graphite and its response to reactor stresses were discussed. The consequences of this behaviour for operational nuclear reactors were found to be significant.
- Young’s modulus studies using time-of-flight techniques were found to be relatively common, but existing methods and analytical techniques frequently conflicted with one another, and the experiments were limited to the bulk graphite material. It was decided that little novel data could be acquired from time-of-flight techniques.
- Existing studies of the damage to the microstructure of graphite by reactor stresses were found to be few in number and limited in depth.
- It was decided that to maximise the novelty and relevance of any data acquired, subsequent experiments into stress-induced damage in graphite should be quantitative in nature and carried out at the microlevel.
• Porosity was found to have a significant effect on the strength and Young’s modulus of graphite. Existing studies into this relationship exhibit a lack of agreement with one another, and attempts to define a quantitative link between the two behaviours have so far seen limited success.

• Imaging experiments were proposed to study stress-induced behaviour of graphite at the microlevel. Confocal microscopy and X-ray tomography were identified as techniques of interest.

• X-ray diffraction experiments were proposed to study stress-induced changes to the crystal structure of the material.
Chapter 3: Sample Preparation and Metrology

This chapter discusses the acquisition, machining and preparation processes that each graphite sample underwent prior to use in the experiments.

Section 3.1 discusses the properties of graphite blocks from which each sample was machined. Section 3.2 discusses the machining processes that were used to produce samples of suitable size and geometry from the large graphite bricks, and the preparation processes that were required to ensure each sample was suitable for its intended purpose. Section 3.3 discusses the basic metrology techniques used to perform preliminary characterisation of each sample, and contains the details of each sample used during the project.

3.1 Material Acquisition

Two large blocks of graphite were provided for the project. One block comprised of quasi-isotropic Gilsocarbon graphite, while the second comprised of anisotropic Pile Grade A graphite. Both blocks were manufactured by British Acheson Electrodes Ltd. (BAEL). Images of the blocks are shown in Figure 3.1 and Figure 3.2.

Figure 3.1: The Gilsocarbon block used as the source material for Gilsocarbon samples during this project. Block dimensions are 23.3 cm long and 10.4 cm wide.
Since manufacture, large amounts of material had been removed from each block for use in other studies, which explains their irregular geometries.

3.2 Sample Preparation

Different experimental techniques require samples to undergo a specific series of preparatory techniques before being suitable for use. This includes the samples being machined to suitable shapes and sizes, undergoing appropriate amounts of surface treatment, and being chemically cleaned. Well established techniques for the machining and preparation of graphite samples were used to produce high quality samples suitable for confocal laser microscopy, X-ray tomography and X-ray crystallography. These processes are discussed in Sections 3.2.1 to 3.2.3 respectively.

3.2.1 Preparation of Confocal Laser Microscopy Samples

A series of samples were machined into cuboids of dimensions between 6x6x6 mm and 12x12x12 mm in the machining shop in the University of Manchester’s School of Mechanical, Aerospace and Civil Engineering. This sample size was determined by two requirements. The first requirement was that the must be small enough to fit
between the jaws of the axial compression rig used to compress the samples, as discussed in Section 4.2.2. The second requirement is less well defined, and relates to the conflict between the sample being large enough to be considered representative of the bulk material, but not so large that the sample becomes impractical, or impossible, to scan using the microscope (for example, due to the image taking up too much memory to fully scan). A method of quantifying the required size for a sample to be representative of the bulk material is discussed in Section 4.6. It is also important that the edges of the sample which come into contact with the jaws of the loading rig are flat and parallel, to ensure the compression is applied evenly across the faces of the sample.

To optimise the samples for imaging, they were polished to provide a flat, defect-free surface which reflected a higher proportion of incoming light, rather than scattering it. A suitable amount of light must be reflected back to the microscope’s detector to produce a high quality image of the sample. By smoothing the samples with progressively finer abrasives, the smaller imperfections were effectively removed from the surface of the samples.

Each sample was mounted on a precision-machined jig designed to keep the sample parallel to the polishing pads, such that the polishing occurred uniformly and that the sample remained flat. Once mounted, the sample was rubbed in a circular motion against a silicon carbide polishing pad. Water was used as a lubricant and to wash away loosened graphite deposits. This grinding process removed the top layers of each sample producing a smoother surface. To ensure no preferential directionality was introduced to its surface, the sample was periodically rotated during polishing.

A series of progressively finer grades of polishing pads were systematically introduced, ranging from a grit of 800 to 4000. With each finer polishing pad, progressively smaller surface imperfections, such as scratches, were removed, and a smoother sample surface was produced.

To ensure the surfaces of the samples were as smooth as possible, a final stage of polishing was performed using felt polishing pads and 1 µm monocrystalline diamond compound. The diamond compound was able to enter open pores greater than size 1 µm at the surface of the sample, while using the soft felt polishing pad produced a smooth surface.
Although the surfaces of the polished samples were rendered smooth, many impurities had been introduced during the process, such as diamond compound and pieces of loose graphite displaced from the surface during polishing. Since graphite is a highly porous medium, these impurities often get lodged in the pores. In order to remove any debris, samples were cleaned using deionised water, followed by twenty minutes in an ultrasonic bath containing acetone. In an ultrasonic bath a transducer generates high frequency ultrasonic waves, which generate ripples in the fluid (in this case acetone) and millions of small vacuum bubbles are produced. The collapse of these bubbles generates high pressures that are effective at removing dirt and surface impurities from the samples. This technique is particularly well suited for removal of residual material from pores within the material.

Once the samples have dried out, they are ready to be used for imaging experiments. Figure 3.3 shows an example of the significant improvements to the smoothness of graphite samples that can be accomplished through the polishing process detailed above.

Figure 3.3: Confocal microscope images of an unpolished region (left) and a polished region (right) of a Gilsocarbon sample. Both images are of the same resolution and size. Polishing produces a significantly smoother and more reflective surface, allowing the microstructure to be observed in greater detail.

For the confocal laser microscopy studies, three types of sample were prepared – one type of Gilsocarbon and two types of Pile Grade A. Two types of PGA were required due to the material’s high degree of anisotropy, and the differences in
material properties in different directions. Half of the PGA samples were machined with the polished surface oriented perpendicular to the grain direction, and half oriented parallel to the grain direction. Since Gilsocarbon is considered quasi-isotropic, no preferential directionality was considered during machining, except for keeping the orientations of the samples consistent.

Figure 3.4 shows some of the samples that were used during the confocal microscopy experiments.

![Sample Preparation and Metrology](image)

Figure 3.4: Typical samples used during the confocal microscopy experiments. Left: a Gilsocarbon sample that sheared horizontally into two pieces. Middle: An unloaded Gilsocarbon sample that is fully intact. Right: A PGA sample that has sheared diagonally.

### 3.2.2 Preparation of X-ray Tomography Samples

X-ray tomography samples have fewer preparatory requirements than microscopy samples since the technique does not depend on reflection of visible light, therefore smooth reflective surfaces are not required. The main requirement is that the samples must be small enough to fit between the jaws of the loading rig, discussed in Section 5.2.2. It is also important that the edges of the sample that come into contact with the jaws of the loading rig are flat and parallel to each other, to ensure the compression is applied evenly across the sample.

As with the confocal microscopy experiments, it was decided that three distinct types of sample were required for this study – one type of Gilsocarbon sample and two types of PGA samples, with half of the PGA samples machined with the long axis parallel to the grain direction and the other half machined perpendicular to the grain direction. The samples were machined into cylinders of height 10 mm and diameter 8 mm by the machining shop in the University of Manchester’s School of Mechanical, Aerospace and Civil Engineering.
In order to optimise the samples for in-situ tomography scanning, the samples underwent a brief polishing process. Unlike for the confocal microscopy experiments, where the samples had to be thoroughly polished to attain a smooth reflective surface, surface roughness is not detrimental for tomography. However, any tilt on the sample during rotation will compromise the reconstruction of the images and result in the formation of a blurred final image. To reduce the risk of this occurring, the top and bottom edges of the samples were polished with silicon carbide polishing pads to a grit of 2000 using the technique detailed in Section 3.2.1.

The samples were then cleaned using deionised water, followed by twenty minutes in an ultrasonic bath containing acetone to remove as many of the impurities as possible from the surface and the pores prior to the tomography scanning. Figure 3.5 shows a typical sample used during the X-ray tomography experiments.

![Figure 3.5: A typical Gilsocarbon sample used during the X-ray tomography experiments. Samples were machined to have a cross-sectional area of 8 mm and height 10 mm.](image)

### 3.2.3 Preparation of X-ray Crystallography Samples

A series of samples were machined into cylinders of diameter 7 mm and height 2-4 mm by the machining shop in the University of Manchester’s School of Mechanical, Aerospace and Civil Engineering. This sample size was partly restricted by the capacity of the stage the samples were mounted to. Sample sizes were also limited by weight, since the motors used to rotate the X-ray diffraction sample stage were known to be weak. However, the low density of graphite meant that this weakness was not an issue, and sample size only needed to be small enough to be accommodated by the sample stage on the X-ray diffractometer.

Compared to the other experimental techniques performed during this project, the X-ray diffraction samples required relatively little preparation. A flat, defect-free surface is useful but not essential for X-ray diffraction, so the samples were polished with a series of progressively finer grades of polishing paper, ranging from a grit of 800
to 2000 (instead of 800 to 4000 for the confocal laser microscopy experiments). No further polishing with monocrystalline diamond compound was required. As previously, the samples were cleansed using deionised water, followed by twenty minutes in an ultrasonic bath containing acetone.

Figure 3.6 shows some of the samples used during the X-ray diffraction experiments. Lastly, Figure 3.7 below shows graphite samples machined for use in confocal laser microscopy, X-ray tomography and X-ray diffraction, allowing a direct comparison of the sizes and shapes of each sample to be made.

Figure 3.6: Typical samples used during the X-ray diffraction experiments. Samples were machined to have a cross-sectional area of 7 mm and height 2-4 mm.

Figure 3.7: The three typical sample geometries used during this project. Left: A thin cylindrical Gilsocarbon sample used for X-ray diffraction. Middle: A Gilsocarbon sample machined into a cuboid used for confocal laser microscopy. Right: A cylindrical Gilsocarbon sample used for X-ray tomography.

3.3 Sample Metrology

The three tables on the following pages display the dimensional properties of each sample used during the project. More samples were produced than would be required for data collection during the project, and spare samples were used for preliminary experiments and testing experimental procedures. Three repeated measurements were made for the weight of each sample, and the average value was recorded and used for any subsequent calculations. Likewise, the length, width and height of each sample were measured three times, used to calculate the volume of the samples, and the mean value of the volume was recorded. For highly anisotropic
materials, the orientation with respect to the grain direction was recorded. Lastly, each sample was assigned a serial number for ease of identification.

Table 3.1 shows the properties of the Gilsocarbon samples, Table 3.2 shows the properties of the PGA samples that were axially loaded parallel to the grain direction, and Table 3.3 shows the properties of the PGA samples that were axially loaded perpendicular to the grain direction.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material</th>
<th>Geometry</th>
<th>Purpose</th>
<th>Mass [g]</th>
<th>Volume [mm³]</th>
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</tbody>
</table>

Table 3.1: Table showing details of the size and dimensional morphology of each Gilsocarbon sample, and information regarding the use of each sample.
### Table 3.2: Table showing details of the size, dimensional morphology and usage of each PGA sample oriented with the loading axis parallel to the grain direction, and information regarding the use of each sample.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material</th>
<th>Geometry</th>
<th>Purpose</th>
<th>Mass [g]</th>
<th>Volume [mm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P001</td>
<td>PGA</td>
<td>Cuboid</td>
<td>Confocal microscopy – methodology testing</td>
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<td>802.35</td>
</tr>
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<td>P003</td>
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<tr>
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<td>Volume [mm³]</td>
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<td>Cylinder</td>
<td>X-ray diffraction</td>
<td>0.338</td>
<td>194.01</td>
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</table>

Table 3.3: Table showing details of the size, dimensional morphology and usage of each PGA sample oriented with the loading axis perpendicular to the grain direction, and information regarding the use of each sample.

3.4 Summary

- The techniques used to prepare and optimise samples for each experimental technique to be utilised in this project were discussed.
- Pile Grade A and Gilsocarbon samples were machined from blocks manufactured by British Acheson Electrodes Ltd.
- Samples to be used for confocal laser microscopy required the largest amount of polishing, due to the need for a smooth, defect-free surface. A progressively finer series of polishing pads were used to produce the smooth surface, and the samples were cleaned in an ultrasonic bath containing acetone.
• Samples to be used for X-ray tomography required less polishing than those for confocal laser microscopy, since the main requirement was that the surfaces of the samples be parallel to ensure uniform loading could occur.

• Samples to be used for X-ray diffraction required only a small amount of polishing, since the technique does not require particularly smooth samples in order to be effective.
Chapter 4: Confocal Laser Microscopy Experiments

This chapter discusses a series of experiments performed using the first of three main experimental techniques selected for use for this project, confocal laser microscopy. The results of these experiments have been published in two peer reviewed publications, as discussed in Appendix A.

4.1 Introduction to Confocal Laser Microscopy

4.1.1 Theory of Microscopy

Optical microscopy is a well established technique for resolving fine details in samples. The optical microscope is a relatively simple device and the operating principles have changed little since its creation in the 17th century.

Figure 4.1 shows the arrangement of a simple microscope. The setup consists of two lenses. The first lens – known as the objective lens – is used to perform an initial magnification of the object. Rays of light travel from the object through a convex lens, producing an image. Through careful control of the focal length of the lens (a measure of how strongly the lens converges light passing through it) and the distance from the object to the lens, it is possible to produce an image that appears larger than the object itself.

The second lens is known as the ocular or eyepiece lens and is used to magnify the image from the objective lens. When the user looks through the ocular lens, a magnified virtual image of the object can be observed. Since the image is magnified, much greater detail can be observed in the image than could be observed in the object by the naked eye.
Figure 4.1 represents a simple design of optical microscope. Additional lenses can be included in the above arrangement to further magnify the image.

The optical microscope is a versatile tool and is ideal for many imaging experiments. However, optical microscopy has a number of flaws that mean the technique is of limited use for the study proposed in Section 2.4.2. The main drawbacks of optical microscopy include:

- Images produced using an optical microscope have a limited depth of field. This is not a problem for very smooth samples or low magnifications where surfaces may appear smooth, but optical microscopy may not be able to produce viable images of rough, morphologically complex surfaces if the roughness exceeds the depth of field. Regions outside this region will appear blurred. Graphite is known to be a highly porous material with complex surface morphology, so attempting to study the surface of graphite using an optical microscope will may in image with blurred regions, particularly in pore regions.

- At high magnifications point objects may be observed as noise-dominated central objects surrounded by a series of rings. These features, known as Airy discs, arise from the limited resolving power the optical microscope. A resolution limit exists beyond which it is not possible to differentiate between two closely spaced Airy discs, meaning it is no longer possible to resolve small
Confocal Laser Microscopy Experiments

objects in the image. This limit is known as the diffraction limit and is defined by Equation (4.1):

\[ d = \frac{\lambda}{2 \, NA} \]  

(4.1)

where \( d \) is the resolution limit, \( \lambda \) is the wavelength of visible light (typically 550 nm, representing green light in the middle of the visible spectrum, is used) and \( NA \) is the numerical aperture of the optical system.

Because of these known deficiencies, it was decided that traditional microscopy was not the most suitable technique for the study of graphite. Through the study of existing literature, it was noted that Bodel [46] and Bakenne [45] have had success using confocal laser microscopy for studies of graphite. Therefore, it was decided that confocal laser microscopy would provide a suitable imaging technique for the experimental programme proposed in Section 2.4.2.

4.1.2 Theory of Confocal Laser Microscopy

Confocal laser microscopy is a method of acquiring three-dimensional surface profiles of opaque materials and full interior imaging of transparent samples. The most significant difference between a confocal laser scanning microscope and traditional optical microscopes is that while the latter can only observe a single depth at any one time, the former can observe a range of depths as far as the light can penetrate. The advantage of this is that out-of-focus fluorescent light is rejected and the final image is very clean [63]. A schematic showing the operation of a typical confocal laser scanning microscope is shown in Figure 4.2.
A laser passes through an aperture and is focused by the objective lens at a specific depth in the object. Scattered and reflected light is recollected by the lens. A beam splitter separates the light and directs part of it toward the detector. A second aperture in front of the detector ensures that only the light coming from the focal point of the object can reach the detector. This light is detected by the photomultiplier tube and is converted into a single pixel using appropriate imaging software.

Typically, the object is mounted on a mobile stage that can move in three dimensions, allowing the laser to scan across the entirety of large samples and produce an image of a two-dimensional ‘slice’ of a fixed height with the brightness of the image proportional to the intensity of the light reaching the detector. This process is repeated at a range of heights, and the series of two-dimensional slices can be combined into a clean, high resolution three-dimensional image displaying the topology of the object.

Confocal laser microscopy is the ideal method of acquiring high resolution, three-dimensional images of the surface of a material. Previous studies [46] have successfully used this method for the study of pore structure of graphite during compression. However, this method is limited in that only open pores which penetrate the surface of the material can be studied; and these pores must be at depths
observable by the microscope (i.e. an open pore originating from a particularly deep crack may not be observable).

4.2 Materials and Apparatus

4.2.1 The Confocal Microscope

Confocal laser microscopy was carried out using an Olympus OLS 4000 Microscope. The microscope allows a range of magnifications from 5x to 250x, with a pixel size of 1.25 x 1.25 µm at 100x magnification deemed suitable for the experiments defined in Section 2.4.2. This resolution represents a compromise between image quality and image size – enough detail must be visible to view the surface microstructure of the materials, but the area studied must be large enough to be considered representative of the bulk material.

The confocal microscope uses a laser to systematically scan across a range of surface planes. For each scan, mobile apertures block out any light that is not in focus, and a single ‘slice’ of focussed image at a specific height is recorded. The series of slices are then combined to form a three-dimensional, high resolution representation of the surface of the sample.

As discussed in Section 4.1, the confocal microscope represents a significant improvement in imaging capabilities over traditional optical microscopes. As well as being able to produce three-dimensional images, the confocal microscope can display the qualitative data in a number of different ways. Data can be represented in two dimensions, similar to that of attainable with a traditional microscope, and in three dimensions. The surface profile data can be displayed in the form of a height map, and can also be converted to greyscale for ease of segmentation.

Figure 4.3 shows the confocal microscope apparatus used for this study.
Figure 4.3: The Olympus OLS 4000 confocal laser microscope. Multiple lenses allow images of a range of magnifications to be produced. The mobile sample stage allows different regions of the sample to be scanned and stitched together with high precision. The sample stage can be controlled automatically by the microscope software, or manually using the controller at the bottom-right of the image.

One particularly useful ability of the confocal microscope is being able to combine a series of scans into one large image using a technique known as stitching. A limitation of all microscopes is that sample sizes are constrained by the capabilities of the apparatus, and increasing the resolution of an image reduces the size of the region that can be observed in it. The confocal microscope is capable of taking a series of separate images at a single resolution and stitching them into a single large image that would not normally be attainable at that resolution. When stitching two adjacent images together, an overlap must be introduced to allow the software to attach the images together with precision, as shown in Figure 4.4. The size of the overlap can be varied, with larger overlaps giving a more accurate stitch but at the expense of reducing the overall area of the stitched region. Using a suitability large stitching overlap region and maximising the quality of the data acquired, images can be produced where the stitched region is not visible by eye. However, even with large overlap regions, processes that track deformation, such as image correlation, may be adversely affected within these regions.
Figure 4.4: Two separate images of a PGA sample stitched together by the confocal microscope software. Image distortion can be seen vertically within the red highlighted area, which represents the overlap region where stitching has taken place.

Many optical microscopes do not have a stitching ability. Although some image analysis packages offer stitching tools, the stitching process is more accurate if the process is performed directly after data acquisition, as opposed to on images that have already been saved and have experienced data losses due to file compression.

4.2.2 The Axial Compression Rig

In order to simulate build-up of stresses in graphite components, it was decided that an axial compression rig would be used to generate the stresses. As discussed in Chapter 2, the technique of applying an axial load to generate stresses in graphite samples is well established, and has been used during a number of studies to investigate the stress-induced variation of the properties of graphite [36, 37, 38, 39, 40, 41, 45, 46].

A Deben Microtester rig, capable of applying axial loads up to 5 kN to samples with a maximum cross-sectional area of 200mm², was selected for these experiments. Tensile and compressive loads can be applied. The Microtester’s integrated software allows real-time tracking of applied loads, sample contraction, as well as quantification...
of applied stresses and strains. The loading process can be paused and the applied load held steady to allow images to be taken by the confocal microscope.

To compress the samples during laser confocal microscopy, a Deben MICROTEST 5 module was used. This apparatus was chosen because it was known to be compatible with the OLS 4000 confocal microscope. Due to the dimensions and capabilities of the rig, sample sizes were limited to widths of 9.5mm and lengths between 12 and 22mm. The available load cells could apply a maximum force of 5 kN, but this is well above what is required – Gilsocarbon and PGA of the dimensions shown above were calculated to fail at around 3.3 kN and 1.2 kN respectively. Figure 4.5 shows the MICROTEST module, while Figure 4.6 shows the module mounted upon the confocal laser microscope sample stage, enabling in-situ data to be collected during load application.

Figure 4.5: The Deben MICROTEST 5 module compressing a Gilsocarbon sample.
4.2.3 Samples and Sample Preparation

As discussed in Section 3.2.1, a series of cuboid samples were machined by the machining shop in the University of Manchester’s School of Mechanical, Aerospace and Civil Engineering. These samples were machined to sizes between 6x6x6 mm and 12x12x12 mm. The samples were polished using progressively finer grades of polishing paper, culminating with the use of felt polishing pads and 1 µm monocrystalline diamond compound to produce a highly smooth and reflective surface. Impurities were removed by placing the sample in an ultrasonic bath containing acetone.

4.3 Preliminary Investigations into Stress-Strain and Deformation Properties of Graphite

The first set of experiments performed were a series of preliminary investigations into the stress-strain behaviour of the graphite samples machined in Section 4.2. Before any studies can be made into any specific microstructural properties of graphite, it is necessary to understand the behaviour of the bulk material.
Therefore, preliminary tests into how the bulk graphite samples respond to the application of stress were performed.

An axial compressive load was applied to a series of samples of different grades and orientations of graphite using the Deben Microtester. The load was cyclically increased and decreased, with each sample experiencing three or four loading-unloading cycles. Each loading cycle increased the applied load to a progressively higher value, culminating just below the expected failure load. The anticipated failure load, $F$, was calculated from values of compressive stress, $\sigma$, and measurements of the cross-sectional area of the samples, $A$, as shown in Equation (4.2):

$$F = A\sigma$$  \hspace{1cm} (4.2)

Using the Microtester’s integrated software, values of applied load and sample contraction were recorded in real time. From this data, values of stress and strain could be calculated. These values were used to gain insight into the fundamental responses of graphite to stresses.

These simple experiments were expected to be useful for a number of reasons:

- The material properties of graphite vary from brick to brick. Therefore, there is no guarantee that data collected from other graphite bricks will be identical to the graphite used in this study. For example, Young’s modulus values for PGA graphite calculated by Nightingale [10] may be different to the Young’s modulus of the PGA samples to be used here.

- Preliminary investigations can be used to confirm that the graphite is behaving as expected and has not, for example, received damage prior to the start of this project. Any severe defects affecting the whole of the brick should be detected following these initial experiments, in which case the brick would be replaced with one that exhibits more typical properties.

- The experiments will provide precise information on the maximum load tolerance of the samples, so during subsequent experiments the samples can be loaded as close as possible to the anticipated failure load, but without causing sample failure. Bodel [46] observed that most of the visible changes to the surface microstructure of graphite occur at 90-100% of the failure load. If Bodel’s observations are correct, then to observe changes to the structure of...
the samples it is necessary to load the samples as close to failure as possible, and these preliminary experiments will enable this.

- Successful completion of preliminary experiments will confirm the viability of the method, will highlight any flaws in the process before the main experiments start and will allow the author to gain experience with using the apparatus.

Three samples were selected for the initial study – one sample of Gilsocarbon and two samples of Pile Grade A. The grain directions of the PGA samples were oriented either perpendicular or parallel to the direction of the applied load, since the material is anisotropic, and the material’s response to a compressive load is expected to differ between orientations. Table 4.1 shows the properties of each sample, the anticipated failure load of each sample calculated using Equation (4.2) and the load cell required to reach the failure load.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material and Orientation</th>
<th>Cross-sectional area [mm$^2$]</th>
<th>Compressive strength [MPa]</th>
<th>Failure load [kN]</th>
<th>Required loading cell [kN]</th>
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<td>G-002</td>
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<td>70</td>
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<td>27</td>
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<td>5</td>
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<td>P-102</td>
<td>PGA - AG</td>
<td>125</td>
<td>27</td>
<td>3.38</td>
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</tbody>
</table>

Table 4.1: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46].

### 4.3.1 Investigation 1: PGA compressed perpendicular to the grain direction

A sample of PGA was compressed with the grain direction oriented perpendicular to the direction of the applied compressive force. Three loading-unloading cycles were performed. Initially, the sample was loaded to 1000 N, and then released to a force of 150 N. This was followed by a second loading cycle to 1650 N and back to 150 N. The final cycle took the load up to 2000 N and back down to 100 N. The maximum compressive force was at 93% of the expected failure load. The loading process is plotted in Figure 4.7 and Figure 4.8.
Figure 4.7: Plot of the applied force against contraction for a PGA sample compressed perpendicular to the grain direction. The first loading-unloading cycle is shown in blue, followed by subsequent cycles coloured red and green. The regular notches in each of the loading cycles indicate when loading was paused for confocal laser microscopy image acquisition.

Figure 4.8: Plot of stress against strain for a PGA sample compressed perpendicular to the grain direction.
Each of the three loading cycles yielded valuable information regarding the deformation behaviour of PGA graphite when compressed against the extrusion direction.

The blue curve shows the initial load to 1 kN and back to 150 N. After an initial ‘bedding in’ period (corresponding to the first 100-200 N), contraction occurred linearly with the applied force. Upon unloading, the sample did not fully recover and a permanent strain of 0.1 mm was observed. Therefore, some of the deformation caused by these relatively low stresses has irreversibly damaged the microstructure of the graphite. The re-expansion was also delayed due to some components of the graphite exhibiting hysteresis.

The red curve shows the sample being loaded up to 1650 N and then back down to 150 N. Given that the force-contraction curve begins to overlap the initial loading curve at around 900 N, this suggests that the recoverable component of the contraction is deforming with hysteresis, similar to that observed during expansion. It was noted that upon reaching the maximum applied load of the first cycle, 1000N, the amount of sample contraction was the same for both the first and second loading cycles. The same behaviour was also observed for the second and third loading cycles. This behaviour is explained by the Kaiser effect, which states that for materials that have previously been loaded, the material will behave elastically during any subsequent reloading until the previous maximum load is reached.

Contraction continued linearly with force up to the peak of 1650 N. When the load was reduced, the sample expanded, eventually returning to the length it exhibited prior to the second loading cycle commencing. All of the deformation that occurred between loads of 1000 and 1650 N was fully recoverable. This suggests that any components that do not fully recover from compression have been fully compressed before the load reached 1 kN, and they exhibit no further permanent deformation.

Lastly, the green curve shows the sample as it was compressed by a force of 2 kN, before being unloaded to a final value of 100 N. The loading behaviour between 1650 and 2000 N was similar to the previous loading cycle, with contraction increasing linearly and exhibiting a time lag. Upon unloading, the sample once again returned to its length as it was after the first unloading. Therefore all deformation occurring between these force values was fully recoverable.
Based on these data, there are two distinct types of deformation occurring in the sample:

- Fully recoverable deformation where, once any compressive forces have been removed, the components exhibit no permanent changes in the direction that the force is applied. This was observed at all levels of compression.

- Non-recoverable deformation, where compression permanently deforms certain components in the sample; and removing the force does not result in full reversal of the damage. This was found to occur only at force below 1 kN. It is not clear whether components affected by this form of deformation are partially recovering or not recovering at all.

Since these two forms of deformation occur over distinct force ranges, it should be possible to determine which components exhibit these behaviours through study of the images produced by the confocal laser microscope.

This research directly conflicts with Bodel’s [46] observations that stress-induced deformation to the microstructure predominantly occurs close to failure. Figure 4.7 shows that deformation is occurring at all applied loads, and that beyond an initial bedding-in period the deformation appears to occur linearly. Since Bodel did not observe these changes during his purely qualitative study of confocal microscopy data, there are three possible explanations for this conflict of results. The first explanation is that the damage is too small to qualitatively observe at the microscale, and that quantitative methods are required at this scale to resolve any structural change. The second is that the changes observed in Figure 4.7 are not occurring at the surface of the material, thus could not have been observed in Bodel’s confocal microscopy images. The third possible explanation is that the samples used in each experiment were sufficiently different to show different microstructural behaviour. However, this is unlikely since Bodel’s samples were machined from the same brick at the author’s samples.

It is expected that the first explanation – that qualitative analysis at this length scale is unsuitable – will explain the conflict between these results and Bodel’s observations. Investigations into the remaining two samples were expected to confirm this hypothesis.
4.3.2 Investigation 2: PGA compressed parallel to the grain direction

A sample of PGA was oriented with the loading axis parallel to the extrusion direction prior to undergoing cyclic loading. The properties of this sample are discussed in Table 4.1.

As before, three loading-unloading cycles were performed on the sample. Initially, the sample was loaded to 600 N, and then released to a force of 30 N. This was followed by a second loading cycle to 12000 N and back to 30 N. The final cycle took the load up to 1800 N and back down to 30 N. The relationship between the applied load and the associated change in sample size is shown in Figure 4.9.

During the initial stages of the first loading cycle, a non-linear force-relationship was observed that corresponded with the ‘bedding-in’ period that was observed during the loading of the PGA-AG sample. After this period, the sample contracted linearly as the load was applied. Comparing the rates of contraction for both PGA samples, the PGA-AG sample exhibited a greater amount of contraction per unit applied load. This suggests that PGA oriented with the extrusion direction perpendicular to the loading
axis is more susceptible to stress-induced contraction than when the extrusion direction is oriented parallel to the loading axis.

When the load was relieved to a token non-zero force, hysteresis was observed and the rate at which the sample recovered was observed to decrease as the load was further removed. The sample did not fully recover and exhibited a small amount of permanent contraction.

Subsequent loading cycles exhibited similar behaviour. Reapplication of the load resulted in nonlinear contraction until the peak of the initial loading cycle was reached, beyond which the relationship between the applied load and the observed contraction appeared linear. Upon completion of the second and third loading cycles, a degree permanent sample contraction was observed as for the first loading cycle.

With the exception of the lower susceptibility to stress-induced contraction, the behaviour of the PGA-AG and PGA-WG samples when exposed to compressive stresses were very similar.

4.3.3 Investigation 3: Gilsoarbon

A sample of Gilsoarbon, whose properties are discussed in Table 4.1, was compressed to a force of 2 kN. The sample unexpectedly failed during loading from 1 to 1.3 kN, the consequences of which are visible during the second loading cycle as shown in Figure 4.10.
Confocal Laser Microscopy Experiments

Figure 4.10: Plot of applied force against contraction for a sample of Gilsocarbon. Four separate loading-unloading cycles are observed, and unexpected failure of the sample was observed during the second cycle, coloured red.

After an initial ‘bedding-in’ period, the sample was found to contract linearly with respect to the applied force. During the first cycle, releasing the applied loads did not allow the sample to fully recover and permanent sample contraction of around 0.09 mm was observed. During the second cycle, part of the sample failed, resulting in sudden contraction without an associated increase in applied force; and release of strains that were building up inside the sample. When the applied forces were removed, partial sample recovery was observed. Unlike previous graphite sample failures, the sample did not shear into separate pieces, and no evidence of the failure was visible on the sample’s surface. It was decided that the loading process would continue, to determine what effect partial sample failure had on the response of the sample to the build-up of stresses.

The third and fourth loading-unloading cycles to 1.6 and 2 kN respectively exhibit broadly similar behaviours. Loading was observed to occur linearly until the failure load was approached, while unloading exhibited hysteresis. Upon removal of load, significant recovery was observed, similar to that experienced by the two PGA samples.

The observation of unexpected failure of the Gilsocarbon sample during the second loading cycle highlights the limitations of qualitative study of stress-induced deformation behaviour. Since there were no visible manifestations at the surface of the
sample of the structural collapse, this behaviour was only observed by utilised quantitative analytical techniques. A qualitative study of the samples, either by eye or using microscopy techniques, would not be adequate for study of this behaviour, which emphasises the importance of acquiring quantitative data.

4.3.4 Conclusions

The initial loading experiments discussed above fulfil a number of requirements and provide valuable information that was used to optimise the main imaging experiments.

The stress-strain behaviour of the PGA and Gilsocarbon graphite were confirmed. Data derived from Figure 4.7, Figure 4.9 and Figure 4.10 were used to confirm that the samples were exhibiting similar material properties as calculated by Nightingale [10] in Table 1.4, ensuring that the graphite blocks provided for the project were behaving as expected.

The loading rig was tested to ensure that it was able to operate to a suitable precision, that it can apply stresses high enough to cause microstructural deformation in the samples, and that, following appropriate sample preparation as discussed in Chapter 3, the graphite samples were suitable for use in conjunction with the loading rig. Of particular importance was that the applied load could be held steady for enough time to acquire a confocal microscopy image. Any large fluctuations in the applied load may cause further sample contraction or relaxation during image acquisition, resulting in a visible discontinuity in the final image. It was found that the applied load could be held steady over a long enough period to allow image acquisition without any further visible dimensional change occurring.

Lastly, through observation of the individual loading cycles, an experimental programme was finalised for the in-situ acquisition of confocal microscopy images during the application of compressive loads. This programme is discussed in Section 4.4.

4.4 Imaging during Loading and Unloading

Following the preliminary experiments discussed in Section 4.3, an experimental programme for the main data collection process was defined. In order to
Confocal Laser Microscopy Experiments

investigate changes in the pore structure due to stress, in-situ images of the surface of the materials during loading are required. The Microtester rig was mounted on the confocal microscope’s sample stage and a series of loading experiments were performed, similar to those discussed in Section 4.3.

For each sample, a single loading sequence was performed, starting with the application of a token non-zero compressive load. After application of a load, the sample was left for three minutes to stabilise before a confocal microscopy scan was performed. After image acquisition, the load was increased and another image was recorded. This process was repeated at progressively higher loads until the sample failed. Images were typically recorded at load intervals of approximately 100 N, starting from a token non-zero force. Applying a force close to zero for the first scan is preferable to actually performing the scan at 0 N because the latter means the sample is unsupported and may move independently of the loading platens.

At each load level twelve separate images were collected of the surface of the samples, which were then stitched together in a 4x3 grid. After stitching the individual images together, the resulting image covered a region of 9510 by 7180 µm of the sample’s surface, which represents an area of 68.3 mm².

Using compressive stresses calculated by Nightingale [10] and Bodel [46], in conjunction with Equation (4.2), Table 4.2 shows the expected failure stresses and the loading cells required to bring each of the three samples to failure.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material and Orientation</th>
<th>Cross-sectional area on loading axis [mm²]</th>
<th>Compressive strength [MPa]</th>
<th>Failure load [kN]</th>
<th>Required loading cell [kN]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-003</td>
<td>Gilsocarbon</td>
<td>41</td>
<td>70</td>
<td>2.87</td>
<td>5</td>
</tr>
<tr>
<td>P-003</td>
<td>PGA - WG</td>
<td>80</td>
<td>27</td>
<td>2.16</td>
<td>5</td>
</tr>
<tr>
<td>P-103</td>
<td>PGA - AG</td>
<td>80</td>
<td>27</td>
<td>2.16</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.2: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46]. Note that the cross-sectional area data provided is along the loading axis, and does not represent the surface being scanning by the confocal laser microscope.
In order to image the entirety of the samples, several individual images of
different parts of each sample were stitched together to produce a single large image.
This stitching process was performed automatically by the microscopy software. To
ensure the individual images were connected as accurately as possible, an overlap of
10% between pairs of images was added. This value was selected based on research
carried out previously by Bodel [43], who found that such overlap would minimise the
stitching artifacts but still allow large areas of data to be observed.

4.5 In-Situ Confocal Laser Microscopy Images

For each sample, twelve stitched images of the full surface of the samples were
collected. Each image was acquired in four different formats – a colour image showing
the surface of the sample, a greyscale image, a colour-based height map that uses a
range of colours to define the height of the surface of the sample, and a contour plot
that also indicates the height of the sample’s surface with respect to a user-defined
baseline. Each of these images is available in both two- and three-dimensions.

The initial set of images shown in

Figure 4.11 exhibit the different ways that the confocal microscope can display the
data. These four images show a sample of Gilsocarbon with no applied load. The top
left image shows a high resolution two-dimensional representation a region of the
Gilsocarbon sample, while the same region is shown in greyscale at the top right. Even
in two dimensions, it is possible to observe the surface of the sample inside the open
pores. A similar resolution image acquired using a traditional optical microscope would
be able to resolve little if any detail inside the pores if the depth of field was not
suitably large, which shows the advantages of using confocal microscopy over
traditional microscopy for analysis of porous materials. The bottom two images show
colour-based height maps of the sample in two and three dimensions, where different
colours indicate that different heights of the surface. In porous materials such as
Gilsocarbon and PGA graphite, the technique is particularly useful for defining the
shapes of pores. Colour-based height maps are of limited use at low resolutions due to
the inability of resolving small pores, so high resolution images like those shown in
Figure 4.11 are required to utilise this technique.
Figure 4.11: Four images of a region of a Gilsocarbon sample, recorded at zero load. Clockwise from top left: Colour image of the sample, greyscale image of the sample, three-dimensional heightmap of the sample, two-dimensional heightmap of the sample. The scale for all images, shown at the bottom left, is the same.

The disadvantage of using such high resolution images is that only small regions of the sample can be observed in a single image. Multiple individual regions can be stitched together to form a single large image, as discussed in Section 4.2.1, but this technique is limited by the memory available in the computer used to control the confocal microscope. Image acquisition and stitching are resource intensive processes, and a typical limit of 20 – 30 images were able to be stitched together at once by the software before typically running out of memory. This enabled suitably large and
detailed images of the samples’ surfaces to be recorded, and did not act as a major limitation to the experimental programme.

The subsequent set of images show the full surface of each sample during the application of a compressive load. With so much data acquired, it is not practical to exhibit all of it here. The images on the following pages exhibit just a small amount of the data that was collected using the confocal microscope during the main experimental programme discussed in Section 4.4, and were selected for being representative of the full data set. For each sample twelve images were acquired. Four images of each sample were selected for display – an image before any load was applied, two images approximately at 40% and 80% of the maximum applied load, and a final image showing the sample close to failure or after it had failed. Figure 4.12 shows the behaviour of the Gilsocarbon sample during loading, Figure 4.13 shows the PGA-AG sample and Figure 4.14 shows the PGA-WG sample.
Figure 4.12: Images of Gilsoarbon taken at a range of applied loads. The compressive load was applied horizontally in the images. The final image shows sample failure.
Figure 4.13: Four images of PGA-AG taken at a range of applied loads. The compressive load was applied horizontally in the images.
Figure 4.14: Four images of PGA-WG taken at a range of applied loads. The compressive load was applied horizontally in the images.
Looking at the full data series, of which the above images represent only a subsection, the limitations of qualitative studies become clear. The graphs of applied load against sample contraction shown in Figure 4.7 show that sample deformation is occurring continuously at all loads, and, beyond the initial bedding-in period, sample contraction appears linearly proportional to the applied load. However, it is very difficult to observe significant changes to the microstructure of graphite by looking at the above images. More changes are visible at large loads than small loads, but overall it would appear that qualitative studies of samples will not provide adequate insight into changes at the microlevel.

In Section 2.2.2.2, a detailed study on stress-induced damage to reactor grade graphite using confocal laser microscopy by Bodel [46] was discussed. His study was purely qualitative in nature. Bodel observed that few microstructural changes were observed during the application of low loads. It was not until the samples began to approach failure that significant amounts of observable microstructural changes began to occur.

However, this represents the limit to the usefulness of qualitative studies. It is difficult to gain additional insight into the response of graphite to stress without using quantitative methods. In Chapter 2 a number of qualitative studies of the behaviour of graphite were discussed, and one of the main conclusions drawn from each of them is that regardless of the quality of the data, a quantitative analysis would allow much more novel observations to be made and enable a greater understanding of the behaviour of graphite to be gained. Through qualitative analysis of the confocal microscopy data, the need for quantitative data analysis was confirmed.

Multiple techniques for the acquisition of quantitative data from images exist. The simplest technique involves using an appropriate image analysis package to define the features of interest — in this case the pores — and run a series of routines and programs that can extract quantitative values that define the morphology of the features. For example, for the images shown in Figure 4.12, Figure 4.13 and Figure 4.14, the area of each pore can be quantified with ease.

A second quantitative image analysis technique is the use of digital image correlation. Digital image correlation is a technique that tracks changes in images that have been recorded at different times in an in-situ environment, for example, during
the application of a compressive load. By taking a pair of images that differ by the application of a known load, digital image correlation software can track the changes that occur between the images. The results can be used to produce a deformation map, quantify local strains, and more. However, the confocal laser microscopy data was not well suited for digital image correlation analysis. The stitching process discussed in Section 4.2.1 is not precise enough to allow the digital image correlation software to adequately quantify the true sample deformation occurring in the stitching region, resulting in invalid outputs. For this reason, it was decided that this project should focus on extracting quantitative data on pore morphology from the images using image analysis software.

4.6 Analysing the Suitability of Sample Geometries

The sizes and geometries of the samples used in these experiments were defined by the capabilities and requirements of the apparatus and the analytical techniques used to study the data. In many cases these requirements conflicted with one another, meaning that compromises had to be made. For example, minimum and maximum sample sizes were limited by the sizes that could be accommodated by the axial compression rig.

The most significant difficulty when determining sample sizes was ensuring the samples were a reasonable approximation of the graphite bricks used in nuclear reactors. Since graphite is highly inhomogeneous and consists of multiple distinct phases, any graphite samples used were required to be large enough to be representative of the bulk scale graphite. If the samples were too small, it is possible that certain features, such as filler particles or fracture paths, may dominate the sample. Any results obtained may not give a true picture of how graphite responds to stress build-up, which would severely limit the usefulness of the data.

Therefore, it was decided that the samples should be approximately an order of magnitude larger than the sizes of the main microstructural features of the material, such as filler particles. The typical sizes of such features are well known, which allowed an initial approximation of a suitable sample size to be made. It was estimated that samples should have a surface for imaging greater than 100 mm² to ensure they are representative of the bulk material. However, a quantitative technique was established
to confirm that samples machined to these geometries would be large enough to be considered representative of the bulk material.

After an initial series of samples were machined, an analysis of the pore structure at a range of length scales was performed with the intention of defining a minimum sample size (or a minimum region of interest, in the event that the whole of the sample surface cannot be studied) above which the sample can be considered homogeneous and hence a suitable approximation of the bulk graphite material.

The open pore structure at the surface of the sample was thresholded and the area at the surface of each pore was calculated, in an experimental technique discussed in greater detail in Section 4.8.1. Up to five subsections of the image were randomly selected at a range of different subsection sizes, and mean pore areas were calculated for each subsection. It was expected that for small regions of interest there would be significant disparity between results for different regions. As the region size increased, the disparities were expected to reduce, eventually reaching point where the location of the region of interest has no effect on the mean pore area. Above this size threshold, the image can be considered homogeneous and representative of the bulk material.

Figure 4.15 shows the results of mean pore area calculations for a range of different sized regions.
Figure 4.15: Variation of mean pore areas for a range of differently sized regions of interest. A quadratic curve is fitted to the data. Five regions of interest were selected for each region size except for the largest size, which corresponded to the entire sample surface, hence was only measured once.

The data in Figure 4.15 is as expected – when small regions of interest are being considered, there is a large degree of variation between different regions. As the region size increases, the variation decreases until a point where the graph plateaus and further increasing the region size has little noticeable effect on the mean pore area.

The data are well described by a quadratic curve, with the gradient of the curve decreasing as the region of interest gets larger. Above a region size of 55 mm$^2$ the best-fitting curve becomes reasonably flat and the scatter of the data points is small. This implies that when the areas being studied are greater than 55 mm$^2$, the regions are suitably large that the microstructural features in the material that create significant inhomogeneity – filler particles, large pores, large fracture paths – have little overall effect on the mean properties of the sample. These features appear to be spread throughout the sample instead of clustering together in specific regions, and are so significantly outnumbered by more regular features (such as small pores) that the effects of large features on mean microstructural properties is limited. In addition, the lack of scatter in the data in Figure 4.17 in regions of interest larger than 55 mm$^2$
suggests that regions of the size are large enough to not be skewed by specific features, such as large outlier pores.

These results suggest that samples with the upper surface having an area of 55 mm² would be suitable for use in the confocal microscopy experiments. However, further increasing the size of the sample would allow more pore data to be collected and make the sample even more representative of the bulk material. Conveniently, samples of the size were also found to be suitable for use with the axial compression rig and the confocal microscope. Hence the samples whose properties were discussed in Table 4.1 were deemed suitable for use in the confocal microscopy experiments.

4.7 Image Segmentation and Segmentation Errors

Images were analysed using Fiji [64], an image analysis package that is particularly suited for the quantitative analysis of microscopy data because it is compatible with user-created plugins. Fiji is an enhanced version of ImageJ, a popular image analysis software package. Fiji contains many additional features not present in ImageJ. The base software has significant capabilities for image analysis, and the gaps or flaws in the software can often be resolved through the use of user-created software. The majority of the analysis of confocal microscopy data was performed using tools provided in the base programme, while user-created plugins became more important for the tomography data analysis discussed in Chapter 5.

Images were imported from the confocal microscope into the Fiji software in the form of JPEGs. A scale was set on the images using data from the microscope, and the images were cropped to fit the dimensions of the samples.

In order to quantify the properties of the pore structure from the confocal microscopy images, the pore structure must be separated out from the binder and filler phases. By splitting the image into distinct phases, the physical properties of each region can be defined. This process is known as segmentation. Due to the large numbers of separate pore regions that will need to be defined, it is important that the segmentation process be automated. Multiple segmentation techniques are available for confocal microscopy images.

The simplest segmentation technique is known as greyscale thresholding, whereby a greyscale image is split into two distinct phases separated by a specific pixel
Confocal Laser Microscopy Experiments

intensity. If a pixel has a lower intensity than the thresholding intensity, the pixel is classed as a black pixel, while if a pixel has a greater intensity than the thresholding intensity, the pixel is classed as a white pixel. When segmenting the pore structure of the graphite samples, the pores are defined using the black pixels, while the non-pore regions are defined using white pixels.

An alternate thresholding technique that is made possible through the use of a confocal microscope over a traditional optical microscope is *height-based thresholding*. Instead of defining a threshold pixel intensity, a threshold height is defined using the three-dimensional confocal microscopy data. Regions above this height can be classed as white pixels and regions below this height can be classed as black pixels.

Both of these techniques can be used for the analysis of the graphite samples. The deep open pores scatter much of the light from microscope instead of reflecting it back into the detector, therefore pore regions appear black. By selecting a greyscale threshold between the dark pores and the lighter binder/filler regions, the porous regions can be defined with precision. The height-based thresholding technique is potentially even more accurate since during polishing the surface of the sample is rendered very smooth and only the pore regions deviate from this surface. However, in order to produce an accurate three-dimensional surface profile, much higher resolution scans are required than were performed. This segmentation technique was rejected since the high resolution scans only cover a very small area of the sample and it was not practical to collect data of such high resolution.

Even though height-based thresholding was rejected, the use of the confocal microscope still enabled much higher greyscale thresholding precision than would be possible using a traditional optical microscope. Since optical microscopes have a limited depth of field, an image of the surface of the sample may not be able to resolve the pore regions, rendering them blurry and with an unclear boundary between pore and binder/filler regions. The confocal microscope can produce high resolution images of the entire surface of the sample, and the distinction between open pore regions and solid regions is well defined. Therefore, greyscale thresholding was used for pore segmentation, taking advantage of the confocal microscope’s abilities to produce a high resolution, three dimensional surface profile.

Images were thresholded using a greyscale thresholding method to separate the open pores from the rest of the surface features. Open pore regions appear black
while non-pore regions appear light grey, so thresholding can segment the images to a high precision. Figure 4.16 shows brightness curves for each sample.

Figure 4.16: Brightness curves for the Gilsocarbon (left) and PGA (right) samples.

In each case there is a narrow peak at low brightness. This peak corresponds to the open pore regions where much of the light is scattered and does not return to the detector. The remainder of the spectrum represents the binder and filler regions. In the Gilsocarbon image a second wider peak is observed, while in the PGA image the first peak drops to a plateau and then linearly decreases to zero with increasing thresholding limit. The lack of a well-defined distinction between pore regions and non-pore regions in the PGA brightness spectrum will make it more difficult to choose an accurate thresholding level.

Figure 4.17 shows this thresholding technique being applied to a subsection of a Gilsocarbon sample.
In practice it is difficult to define a value for the thresholding limit because there is often no single correct value – particularly for morphologically complex materials such as graphite. There is a continuum of threshold limits that provide reasonable definitions of the extent of the pore structure; therefore a systematic error is introduced into any calculation of pore properties.

In order to quantify these errors and ensure that the most appropriate thresholding limits were used, a single confocal microscope image was thresholded at a series of different values. From this thresholded data the value of mean pore area was calculated, the methodology for which is discussed in detail in Section 4.8.1. For each image, an upper and lower limit was defined for the region where the thresholding appears reasonable. This was a qualitative judgment made by eye. The thresholding value directly in the middle of the upper and lower limit was then defined as the thresholding level.

The error introduced during the thresholding process is thus defined as the difference between the thresholding level and the upper and lower bounds. This was
Confocal Laser Microscopy Experiments

converted to a percentage value to be used to calculate the errors for other images. This process was repeated for both PGA and Gilsocarbon. Figure 4.18 shows the variation of mean pore area in Gilsocarbon at a range of thresholding limits. From this graph the thresholding level was defined as 40 and the errors introduced during thresholding were calculated to be +7.94% and -6.69%. Figure 4.19 shows the variation of mean pore area in PGA at a range of thresholding levels. From this graph the thresholding limit was defined as 37 and the errors introduced during thresholding were calculated to be +7.27% and -5.65%.

Figure 4.18: Graph showing variation of mean pore area at different thresholding levels for Gilsocarbon graphite. The lower and upper bounds for reasonable thresholding were 37 and 43 respectively, resulting in a thresholding limit of 40 and errors of +7.94% and -6.69%. These errors are shown on the graph for each mean pore area value.
Figure 4.19: Graph showing variation of mean pore area at different thresholding levels for PGA graphite. The lower and upper bounds for reasonable thresholding were 34 and 40 respectively, resulting in a thresholding limit of 37 and errors of +7.27% and -5.65%. These errors are shown on the graph for each mean pore area value.

The difference in variation of mean pore volume with increasing thresholding limit for PGA and Gilsocarbon was unexpected. In Gilsocarbon, increasing the thresholding limit reduced the mean pore area. However, increasing the limit for the PGA sample resulted in an increase in mean pore area.

For PGA graphite, increasing the threshold limit introduced many new small pores. But this effect was diminished by the fact that pores are much more numerous and closer in proximity in PGA graphite than in Gilsocarbon. Raising the thresholding limit, even by a small amount, resulted in separate pores merging together, reducing the number of distinct pores but increasing their mean size. In Gilsocarbon the pores are much more spaced apart. Increasing the threshold limit introduced many new small pores, but did not result in the merging of many existing pores. Therefore, the mean pore area was observed to reduce.
4.8 Pore Dimensional and Property Analysis

Once the images were successfully segmented to define the pores, it was possible to perform a number of quantitative analyses on each pore with the intention of determining how the pores respond to the development of stresses. The importance of the pore structure to the overall strength and behaviour of graphite moderator components is well established [30, 52, 56, 58], and the need to understand how pores affect the behaviour of graphite components has already been discussed.

Fiji contains a number of functions and tools that can be useful to acquire numerical data from the confocal microscopy images and quantify a number of different pore properties. The properties selected for study were:

- **Pore areas.** This is defined as the cross-sectional area of open pore in the surface plane of the sample. Pore areas are the best indicator of the size and extent of the pore structure that can be attained without using fully three-dimensional data. An understanding of the sizes of pores and the total porosity in a sample will yield valuable information on the sample’s strength and integrity.

- **Pore eccentricity.** Eccentricity is a measure of how much an object deviates from circularity. Pores of different eccentricity will exhibit different resistances to stress-induced damage, and effects of variation of pore eccentricity on material properties of graphite is an important but little studied process.

- **Pore orientation.** This is a measure of how the pores are oriented in the sample and how strong the ordering is. As discussed in Section 1.5, orientation of pores may be introduced into graphite materials during the manufacturing process, which will have an impact on the overall strength of the material.

- **Pore angularity.** Angularity is a measure of how smooth the exterior edges of a feature are. Multiple definitions of angularity exist and there are many accepted methods of calculating it. The relevance of this parameter on component strength and a novel technique for calculating a measure of angularity is discussed in Section 4.8.4.

- **Pore separation.** This measures the spacing between pores. Therefore, a study of pore separation could also be considered as a study of the deformation behaviour of the binder and filler phases. Two distinct techniques were used for
Confocal Laser Microscopy Experiments

this study – a nearest neighbour analysis that quantifies the shortest distance between each pore and the nearest separate pore; and a Voronoi analysis that defines each pore using a Voronoi cell.

The above properties were calculated for each pore observed in the images. By studying these properties at a range of applied loads, a greater understanding of the behaviour of the bulk material in response to stresses was gained.

4.8.1 Pore Areas

After performing the segmentation process discussed in Section 4.7, each individual pore had been successfully defined. The ‘analyse particles’ tool in Fiji was used to quantify the areas of each individual segmented region. This tool works by calculating the number of pixels that each segmented region is comprised of. Once the scale of the image was been defined using the resolution of the confocal microscope, the area of each individual pore was calculated.

At 50x confocal microscope magnification the images exhibited a resolution of 2.5 µm. It is not possible, however, to study the pore structure at this level, since small pores with sizes of the order of a few pixels will not be adequately resolved. Therefore, when thresholding the images, a selective cutoff was applied to ensure that the pores studied were not dominated by errors due to the pixel size. By studying the percentage errors for pores comprised of increasingly fewer pixels, it was decided that a size cutoff of 50 µm² represented a suitable compromise between removing features too small to be accurate representations of the actual pores and minimising data loss on small features. Pores smaller than this cutoff were rejected from further study.

There are two sources of error that reduce the accuracy of the pore area calculations. The first error is the error due to thresholding, discussed in Section 4.7. The second error is due to the resolution of the images. Each segmented pore region is comprised of a number of pixels, and once thresholded each pixel can only be in one of two states – defining a pore or not defining a pore (or more simply: black or white). For a feature that appears 5 pixels in length, an error of half a pixel exists at each end. Therefore the true length of the feature could be between 4 and 6 pixels inclusive. This behaviour must be taken into account when determining the pixel size error on each
feature. However, due to some pores exhibiting complex, irregular shapes, calculation of this error is often complicated.

The most suitable method of calculating errors on pixel size for complex pores is to use an approximation for the shapes of the pores. It was decided to fit an ellipse to each pore using the ellipse fitting function in Fiji. An ellipse is a regular shape whose area $A$ can be defined in terms of the ellipse’s semi-major and semi-minor axes, $a$ and $b$ respectively:

$$ A = \pi ab $$

Therefore the error on the area, $\sigma_A$, can be calculated using:

$$ \sigma_A = \pi \sqrt{\frac{(\sigma_a)^2}{a} + \frac{(\sigma_b)^2}{b}} $$

Each pixel has a diameter of 2.52 µm, so the error on $a$ and $b$ is double the pixel size, 5.04 µm, as shown above.

The error due to pixel size was combined in quadrature with the error due to thresholding, to calculate the total error on pore area.

Pore areas were calculated for each sample at a range of applied axial loads. Figure 4.20 shows the initial range of pore areas observed at zero load in a Gilsocarbon sample, and Figure 4.21 shows the range of pore areas observed in a PGA sample at zero load.
Figure 4.20: Graph showing pore area distributions for a Gilso carbon sample with zero load applied. Data are grouped into bin size of 10 µm². No data is available for pores below 50µm². In each case a tail extends to the right, beyond the region shown above. The visible range in each graph corresponds to over 99% of the data points.

Figure 4.21: Graph showing pore area distributions for a PGA sample with zero load applied. Data are grouped into bin size of 10 µm². No data is available for pores below 50µm². In each case a tail extends to the right, beyond the region shown above. The visible range in each graph corresponds to over 99% of the data points.
The frequency of pores of a given surface area appears to be a function of area, and Gilsocarbon and PGA exhibit broadly similar pore area distributions. Frequency of a given size of pore decreased with increasing size, and a long tail to the right is present. This suggests that there is a very strong bias towards small pores, and emphasises the importance of obtaining high resolution images for the study of pore structures in graphite.

In order to clarify the relationship between pore area and frequency, the data were plotted on logarithmic axes, as shown in Figure 4.22.

![Figure 4.22: Pore area distributions for Gilsocarbon and PGA graphite, plotted on logarithmic axes. A power law has been fitted to each data series.](image)

On a logarithmic scale the relationships appear to be well defined by linear fits, which correspond to a power law behaviour on a linear scale. This type relationship is also known as a \textit{fractal distribution}. A fractal distribution can be defined for a number of objects \(N_i\) with dimension \(r_i\) such that:

\[
N_i = \frac{C}{r_i^D}
\]  

(4.5)
where $C$ is a constant or proportionality and $D$ is a parameter known as the fractal dimension. In the case of Figure 4.22, the fractal dimensions for Gilsocarbon and PGA are -1.675 and -2.211 respectively.

Pore areas in PGA graphite decrease in frequency with increasing size at a greater rate than in Gilsocarbon, but is only at pore areas above $410\mu m^2$ that pores of a specific area become more numerous in Gilsocarbon than in PGA. This suggests that the mean pore area will be greater in Gilsocarbon than in PGA, and that the behaviour of the bulk pore structure is more likely to be skewed by a small number of large pores in Gilsocarbon than in PGA.

At zero applied load, the total porosity of the samples were calculated. Porosity was found to comprise 15.6% of the Gilsocarbon sample and 22.8% of the PGA sample. Using density values from Table 1.4 and mass and volume measurements of the samples, the expected porosities for Gilsocarbon and PGA were 18.3% and 24% respectively. Minor differences between the measured and theoretical values were expected due to the inhomogeneity of graphite across different bricks, and the observed porosity values suggest that the segmentation process has resulted in a reasonable definition of the pore structures of the samples.

In order to determine how the development of internal stresses affect the areas of pores, mean pore area values were calculated for each applied load. These results are shown in Figure 4.23. Data for three samples are shown – one Gilsocarbon sample, one PGA sample with the grain direction parallel to the loading direction and one PGA sample with the grain direction perpendicular to the loading direction. In each case the samples had images taken initially at zero load, then increasing to around 95% of the anticipated failure load calculated using Equation (4.2).
Confocal Laser Microscopy Experiments

Figure 4.23: Graph showing variation of pore areas at the surface of PGA and Gilsocarbon samples during the application of an axial load.

It is important to note that the absolute values of the mean pore area are of limited use – the values are affected by the image segmentation and analysis techniques. The important observations and conclusions that can be drawn from Figure 4.23 are the relative changes in mean pore area, i.e. how the mean value changes with increasing load, and how the behaviour of different samples vary. Therefore, the analyses of any mean parameters calculated in this project will typically focus on the variation of such values between different samples and different applied loads.

In Gilsocarbon, mean pore areas were found to decrease linearly during the application of compressive loads. This suggests that pores are closing as a result of the applied load; and that pore closure occurs at a fixed rate at all loads. This conflicts with previous research by Bodel [46], who performed a purely qualitative study of changes to the pore structure and only observed minor changes to the microstructure at low loads, with the majority of the deformation occurring at high loads approaching failure.

Observed at high loads, new porosity was created in the filler particles, and these pores were typically relatively small. At the same time, some existing lenticular porosity in the filler particles was observed to grow, increasing their mean size. The net result is an increase in frequency of small lenticular pores and a mean increase in the
size of lenticular pores that were already present in the filler particles prior to loading. These behaviours combine to produce a larger than average decrease in mean pore area.

In PGA graphite, the average pore area was smaller than that in Gilsocarbon. This corroborates the prediction made using the data in Figure 4.22. In both orientations the loading-induced pore shrinkage appeared to occur linearly as with Gilsocarbon, but at a different rate.

Compressing a PGA sample perpendicular to the grain direction (i.e. the ‘PGA-AG’ sample) reduced the mean pore area. The rate of change of pore area with increasing load was greater than that observed in Gilsocarbon. This was expected since PGA has a lower stiffness than Gilsocarbon. The reason for this is that in the PGA-AG sample the long thin filler particles, and the pores within them, are oriented with their long axis perpendicular to the loading direction. Applying a load can compress pores of this shape and orientation easily.

The PGA-WG sample, when compressed, exhibited a smaller reduction in mean pore area than the PGA-AG sample, due to the increased stiffness as a result of the filler particles being oriented parallel to the loading direction. The pores are much more resistant to dimensional change in this orientation, giving the bulk material increased strength. Hence a greater compressive force is required to cause the same amount of pore closure in PGA-WG compared to PGA-AG.

4.8.2 Pore Eccentricity

Eccentricity is a measure of how much a feature deviates from circularity. It is defined on a scale from zero to one, where the eccentricity of a circle is zero, the eccentricity of a straight line is one and the eccentricity of any other shape lies between these two values.

Pore eccentricities were calculated by fitting ellipses to each individual thresholded pore region, determining the semi-major and semi-minor axes of the ellipse, and then calculating the eccentricity of the ellipse using Equation (4.6).

\[ e = \frac{\sqrt{a^2 - b^2}}{a} \]  
(4.6)
where \(a\) and \(b\) are the semi-major and semi-minor axes of the ellipse respectively, and \(e\) is the eccentricity.

The ellipse fitting process is performed automatically by the Fiji software. The criteria that the software uses when fitting an ellipse to a feature are:

- The centroid of the original object and the fitted ellipse are at the same location.
- The orientation of the object and the fitted ellipse, defined by calculating the major axis of the object, are the same.
- The area of the object and the fitted ellipse are equal.

The effectiveness of this method is limited due to the inability to accurately fit ellipses to structurally complex pores. In order to determine the quality of each individual fit, the perimeter of the actual pore was calculated and this was compared to the perimeter of the fitted ellipse, \(p_e\), calculated using Ramanujan’s equation [65]:

\[
p_e = \pi \left[ 3(a + b) - \sqrt{(3a + b)(a + 3b)} \right] \tag{4.7}
\]

where \(a\) and \(b\) are the semi-major and semi-minor axis lengths respectively. The ratio of true perimeter to fitted perimeter was calculated, with a perfect fitting ellipse producing a result of 1. The further away the ratio gets from this value, the poorer the fitting quality of the ellipse. Thus by selecting data within a specific range of ratios, pores with badly fitting ellipses (and hence poor estimates of eccentricity) were eliminated. An acceptable fitting range of 0.75-1.25 was selected through visual analysis of the images, which eliminated approximately 15% of the pores.

The main source of error for eccentricity calculations is the error due to pixel size discussed in Section 4.7. To calculate this error, Equation (4.6) can be rewritten in the form shown in Equation (4.8).

\[
e = \left(1 - \frac{b^2}{a^2}\right)^{\frac{1}{2}} \tag{4.8}
\]

where \(a\) and \(b\) are the semi-major and semi-minor axes of the ellipse respectively, and \(e\) is the eccentricity. Defining a new variable \(X\):
The error associated with $X$ due to pixel size is:

$$\sigma_x = X \sqrt{\left(\frac{2\sigma_b}{b}\right)^2 + \left(\frac{-2\sigma_a}{a}\right)^2}$$  \hspace{1cm} (4.10)

Hence the error associated with eccentricity due to pixel size is:

$$\frac{\sigma_e}{e} = \sqrt{\frac{\left(\frac{1}{2} \sigma(1-X)\right)^2}{(1-X)}}$$  \hspace{1cm} (4.11)

$$\frac{\sigma_e}{e} = \sqrt{\left(\frac{\left(\frac{2\sigma_b}{b}\right)^2 + \left(\frac{-2\sigma_a}{a}\right)^2}{(1-b^2a^{-2})}\right)^2}$$  \hspace{1cm} (4.12)

$$\sigma_e = \frac{1}{2} \left(\frac{\left(\frac{2\sigma_b}{b}\right)^2 + \left(\frac{-2\sigma_a}{a}\right)^2}{(1-b^2a^{-2})}\right) e$$  \hspace{1cm} (4.13)

Values of the mean pore eccentricity at each load were calculated before and after the ellipse fitting criteria were applied. It was found that at each load studied, removing the eccentricity values derived from badly fitting ellipses increased the mean value of eccentricity, as shown in Table 4.3. Therefore the pores that are poorly defined by ellipses were predominantly of low eccentricity. Further properties of these pores were studied by taking the thresholded images and removing all pores that were described by well-fitting ellipses, leaving only the pores that cannot be reasonably defined by ellipses. These pores were mainly found in the filler regions of the sample and were spread across the whole of the bulk sample. These pores were also found to
be larger than average, with the mean area of the poorly-defined pores greater than the mean pore area in each sample.

<table>
<thead>
<tr>
<th>Load [N]</th>
<th>Eccentricity – original</th>
<th>Eccentricity - adjusted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.782</td>
<td>0.811</td>
</tr>
<tr>
<td>500</td>
<td>0.785</td>
<td>0.816</td>
</tr>
<tr>
<td>1500</td>
<td>0.792</td>
<td>0.825</td>
</tr>
</tbody>
</table>

Table 4.3: Mean pore eccentricity values before and after the ellipse fitting criterion was applied. Mean eccentricity increased upon application of the fitting criterion.

Pore eccentricities were initially studied with no applied load. For each sample, the eccentricity of every pore that was well defined by an ellipse was calculated. The results were plotted on a histogram to show the frequency of pores observed at each degree of eccentricity, as shown in Figure 4.24. The number of pores observed at each eccentricity was plotted as a percentage of the total number of pores in the sample.

Figure 4.24: The range of pore eccentricities observed in Gilsoarbon and PGA samples with zero applied load. An eccentricity of zero represents a perfect sphere, while progressively larger values indicate the pore has an increasingly large aspect ratio. Pores defined by poorly-fitting ellipses have been removed.
All three samples exhibit very similar properties of pore eccentricities. Each sample exhibits a unimodal distribution, with a strong bias towards highly eccentric pores. The modal values range from 0.88 to 0.94, and in each case the mean pore eccentricity is lower than the mode, which is indicative of negative skew. The PGA samples were observed to have a sharper peak and a narrower tail than the Gilsocarbon sample. These results agree with the studies into pore eccentricity by Kane [56], and further disprove his original hypothesis that a bimodal distribution would be observed due to the different behaviours of binder pore and filler pores.

The relationship between pore eccentricity and pore area was studied by plotting a scatter graph, as shown in Figure 4.25.

Figure 4.25: Scatter graph showing the area and eccentricity of each pore (well defined by an ellipse) in the Gilsocarbon sample.

These data suggest that the greater a pore’s size, the more eccentric it is likely to be. Small pores, such as those at the lower end of the resolvable scale, exhibit a much greater range of eccentricities than the larger pores. There appears to be a range of pore areas from 50 – 5000 µm² where the area of a pore is uncorrelated with its eccentricity. Above this range, it appears that larger pores are typically more eccentric than smaller pores. Plotting a line of best fit confirms the positive correlation between
pore area and pore eccentricity across the whole data set, but the $R^2$ value is so poor that such a line is of little statistical merit.

After removal of the pores that were poorly described by ellipses, values of mean pore eccentricity were calculated at each level of applied load. Figure 4.26 shows the variation of mean pore eccentricity with increasing applied load for the PGA and Gilsocarbon samples.

![Figure 4.26: Variation of mean pore eccentricity for PGA and Gilsocarbon graphite during the application of axial compressive loads.](image)

Gilsocarbon was predominantly found to contain highly eccentric pores. At zero load, the mean pore eccentricity was 0.811. As the sample was loaded, the mean eccentricity increased linearly up to 0.825 at 37 MPa, representing 95% of the expected failure load.

This behaviour is explained by the varying degrees of deformation occurring in pores of different orientation. Bodel [46] has shown that pores oriented in the direction of the applied load are much stiffer and more resistant to change than pores oriented perpendicular to the loading direction. Gilsocarbon is manufactured to be semi-isotropic, with no preferential pore orientation; hence pores of all orientations were present in the sample. When the load was applied, pores oriented perpendicular
to the loading axis were less resistant to loading-induced collapse and exhibited a relatively large increase in eccentricity. The pores oriented parallel to the loading direction were stiffer and more resistant to dimensional change, and exhibited a smaller reduction in eccentricity. These competing changes resulted in a net increase in mean eccentricity. This behaviour is shown in Figure 4.27.

Figure 4.27: Schematic showing example behaviour of different orientations of highly eccentric pore, and the effects of axial loading upon their eccentricity. Arrows indicate the loading direction.

The mean eccentricity changes at high loads may also be affected by changes in the filler particles. Bodel [46] has shown that when Gilsocarbon is loaded to within 10% of failure, new lenticular pores are created and existing pores increase in length in the filler particles. This growth and extension of highly eccentric pores would suggest an above average change in mean pore eccentricity at very high loads. However, this behaviour is not definitively observed in Figure 4.26, suggesting that the mean eccentricity changes caused by growth of pores in filler particles are small.

For the PGA-AG sample compressed perpendicular to the extrusion direction, mean pore eccentricity at zero load was 0.8005, slightly lower than in Gilsocarbon. When axially loaded, the eccentricity increased linearly as shown in Figure 4.26. The steeper gradient than in the Gilsocarbon sample suggests the pores are more susceptible to deformation than those in Gilsocarbon. This was expected due to the lower stiffness of PGA graphite as shown in Table 1.4, and due to the orientation of the needle-like pores perpendicular to the loading direction.

As discussed above, pores aligned perpendicular to the loading axis are less stiff than if they were oriented parallel to the axis. In PGA graphite, filler particles
Confocal Laser Microscopy Experiments

containing needle-like pores are oriented preferentially in the grain direction during the manufacturing process [46]. Pores in the binder matrix show little preferential direction or shape. The net effect when compressing the sample perpendicular to the grain direction is dominated by the collapse of long, thin pores, resulting in an increase in eccentricity.

By comparison, the PGA-WG sample exhibited a much smaller increase in mean pore eccentricity when compressed parallel to the grain direction, so the long thin pores oriented parallel to the loading axis were more resistant to change. However, the compression of these pores should reduce their eccentricity, which suggested that a decrease in mean eccentricity would be observed. However, Figure 4.26 shows that the opposite – a slight increase in mean eccentricity – has occurred.

The observed increase is believed to be caused by the influence of pores in the binder phase. Pores with no preferential orientation were observed in the binder phase in both PGA-AG and PGA-WG. Due to the resistance to change of the pores in the filler particles in PGA-WG, the binder phase pores had a greater effect on mean eccentricity in PGA-WG than in the PGA-AG sample. A relatively large increase in mean eccentricity was observed in the perpendicular-oriented pores, while a relatively small decrease in mean eccentricity was observed in the parallel-oriented pores. The net result is a slight increase in mean eccentricity as the applied load was increased, as shown in Figure 4.28.
Figure 4.28: Loading-induced variation of mean pore eccentricity in PGA-WG. Three sets of data are shown – all pores, pores oriented within ±10° of the loading axis (parallel oriented) and pores oriented 80-100° from the loading axis (perpendicular oriented).

4.8.3 Pore Orientation

Pore orientations were calculated by defining the principal axis of each pore and calculating the angle formed between the principal axis and the loading axis. The principal axis was calculated using the ellipses fitted to each pore as discussed in Section 4.8.2, and defining the principal axis as the major axis of the ellipse. The orientation angle of each pore with respect to the loading axis was an angle between 0° and 179°, defined anticlockwise about the loading axis, as shown in Figure 4.29.
The error due to pixel size associated with the orientation angle must once again be taken into account. The orientation angle $\theta$ can be defined in terms of lengths $L$ and $H$, shown in Figure 4.29, such that:

$$\theta = \tan^{-1} \frac{H}{L}$$  \hfill (4.14)

Defining a variable $X$ such that:

$$X = \frac{H}{L} \quad \text{and} \quad \theta = \tan^{-1} X$$  \hfill (4.15)

The error on $X$ can be calculated using:

$$\frac{\sigma_X}{X} = \left( \frac{\sigma_H}{H} \right)^2 + \left( \frac{\sigma_L}{L} \right)^2$$  \hfill (4.16)

Therefore the error associated with $\theta$ is defined as:

$$\frac{\sigma_\theta}{\sigma_X} = \frac{d}{dX} (\tan^{-1} X) = \frac{1}{1 + X^2}$$  \hfill (4.17)
Hence:

\[
\sigma_\theta = \frac{1}{\left(1 + \left(\frac{H}{L}\right)^2\right)} \sqrt{\left(\frac{\sigma_{H}}{H}\right)^2 + \left(\frac{\sigma_{L}}{L}\right)^2 \frac{H}{L}}
\]  
(4.18)

Histograms were plotted to show the range of pore volumes observed in the PGA and Gilsocarbon samples at each level of applied load. The results for the Gilsocarbon sample are shown in Figure 4.30 and the results for the PGA sample are shown in Figure 4.31.

![Figure 4.30](image)
Figure 4.30: Pore orientation distribution in the Gilsocarbon sample at a range of applied loads.
Confocal Laser Microscopy Experiments

Figure 4.31: Pore orientation distribution in the PGA-AG sample at a range of applied loads, with a best fitting third order polynomial curve applied.

In the Gilsocarbon sample the distribution was observed to be largely uniform, with the exception of a wide peak observed at 25° and a series of very narrow peaks at 45°, 90° and 135°. These results were unexpected since Gilsocarbon is manufactured to be quasi-isotropic. The fact that the peaks at 45°, 90° and 135° are very narrow – approximately 2° across – and evenly spaced suggests that these peaks are erroneous and are not truly representative of the pore structure of the sample.

In the PGA-AG sample, the angle distribution was unimodal with the peak at 74°, and the data were fitted to a third order polynomial curve. This was expected since the pores gain preferential orientation during the extrusion direction, with the peak expected to be at or around 90°. With the mode being observed at 74°, preferential directionality in the material is confirmed. However, a series of sharp, narrow peaks were observed at 45°, 90° and 135°, as was seen in the Gilsocarbon sample. This strongly corroborates the theory that these features are being introduced during the data analysis process and are not present in the actual samples.

Further analysis of the pore orientation data showed that a large proportion of the pores oriented at 45°, 90° and 135° were very small, typically comprising fewer
than 15 pixels. It was found that due to the way the ellipse fitting program works, certain pixel distributions of pixels would produce ellipses oriented at the above angles. Rectangular pixel arrangements resulted in ellipses oriented at 0° and 90°, while square arrangements resulted in ellipses oriented at 45° and 135°. For larger pores comprised of more pixels, it was much rarer to observe perfectly square or rectangular pixel arrangements. Therefore it was proposed that the pore orientation analysis cannot be accurately applied to small pores.

The problems with trying to quantify behaviour of small pores described by a small number of pixels were discussed in Section 4.8.1. For the same reasons it was decided to apply the pore area cutoff of 50 µm² again, to eliminate pores that are so small that the orientation analysis fails.

Having applied the selective cutoff, pore orientations were once again studied at a range of loads in PGA and Gilsocarbon. Figure 4.32 shows the frequency of pores oriented at each angle in 2° intervals at with no load applied.

![Figure 4.32: Pore orientation histograms for PGA and Gilsocarbon samples at zero load. The PGA-AG data has a third order polynomial curve fitted to it.](image)
Looking at Figure 4.32, it is clear that rejecting small pores from the analysis has removed the sharp peaks at 45°, 90° and 135°. This suggests that the pore area cutoff of 50 µm² is suitable for the analysis of pore orientations.

In Gilsonite, the pore angle distribution is largely uniform, with the exception of a wide peak observed at 25°. This was unexpected since Gilsonite is manufactured to be quasi-isotropic [10]. Outside of the peak region, the distribution of pore angles is largely uniform. The wide peak was believed to represent a preferred orientation for the material introduced during the manufacturing process. Despite the attempts to ensure isotropy of the material during manufacturing, it is proposed that the moulding process that Gilsonite undergoes may introduce the observed degree of anisotropy. During moulding, the material is compressed between two plates and is cast into the required shape. This compression process will deform the filler particles and the pores within them. Since the pores in Gilsonite’s filler pores exhibit no preferential directionality, the deformation of the filler particles during moulding may introduce a small degree of preferential orientation in one specific direction. However, this hypothesis cannot be confirmed without studying Gilsonite that has not undergone the moulding process.

In the PGA-AG sample, the orientation angle distribution was unimodal with the mode at 74°, and the data were fitted to a third order polynomial curve. Due to the extrusion process during manufacturing, the pores in PGA samples were expected to show preferential orientation in the extrusion direction, which would be corroborated by the observation of a peak at 90°. With the mode being observed at 74°, the anisotropy of the material is confirmed, as well as a weak preference for pore orientation in the grain direction.

It was anticipated that the PGA-WG data would exhibit a similar trend as PGA-AG sample, but shifted by 90°. This behaviour was expected since the sample has simply been rotated by 90° compared to the previous data. However, the actual data is slightly different to this prediction, with a sharper peak in the PGA-WG data than the PGA-AG data. The mode was observed at 158° and the minimum at 94°, but the data in its current form could not be described well by any low order polynomial.

In order to apply an accurate fitting curve, the data between 156° and 178° were represented as values between -2° and -20°. The PGA-WG data are plotted in this form in Figure 4.33.
Figure 4.33: Pore orientation histograms for the PGA-WG sample at zero load. The data has a second order polynomial curve fitted to it.

The data displayed in this manner are best described by a second order polynomial curve (as opposed to the third order polynomial curve used to describe the PGA-AG data in Figure 4.32, but the data in the region of 140° - 166° exhibit a greater rate of change than was expected, and no low order polynomial fitting curve describes this part of the data particularly well.

Studying absolute values of mean pore orientation is of limited usefulness for this property. Despite the significant differences in the distribution of orientations, PGA-AG and PGA-WG exhibit similar values of mean pore orientation as shown in Figure 4.32; and the GilsoCarbon angle distribution is not well defined by a mean value. However, relative changes between observed mean values at different loads will show any overall trends of rotation. Figure 4.34 shows the percentage change of mean pore orientation at a range of loads.
Applying a load to the Gilsocarbon sample caused the mean orientation angle to decrease linearly. A small mean clockwise rotation of pores was therefore observed. The extension of existing pores and growth of new lenticular pores at high loads, as discussed in Section 4.3, was expected to have little effect on the mean particle orientation. This is because the pores in question are predominantly observed in filler particles and have a lenticular, shell-like structure. Through observation of the filler particles, changes to these pores appear to have little preference in direction during particle contraction. This hypothesis was confirmed by the lack of any above-average changes to the orientation angle as shown in Figure 4.34.

Applying a load to the PGA-AG sample reduced the mean orientation angle, which again signifies a mean clockwise rotation of pores. However, the change in angle per unit stress was lower than that in Gilsocarbon. This was unexpected since PGA is weaker than Gilsocarbon, hence was expected to be more susceptible to loading-induced microstructural changes. A possible explanation for this behaviour is that pore shrinkage and pore rotation are competing effects. In the relatively weak PGA, the
pores may preferentially shrink when loaded. For rotation to occur the pores must retain their structural integrity, which explains why in the stronger Gilsocarbon, a greater degree of rotation and a smaller degree of pore shrinkage is observed. If pore shrinkage does compete with pore rotation, it is proposed that the amount of each behaviour observed depends upon the stiffness of the material. Samples oriented in directions that maximise their stiffness should exhibit less pore shrinkage and more pore rotation, and samples at weaker orientations should exhibit greater pore shrinkage coupled with less pore rotation.

Applying a load to the PGA-WG sample caused an overall clockwise change in the mean pore orientation angle. The observed rotation per unit applied load is slightly greater than that observed in the PGA-AG sample. This was expected since PGA-WG is less stiff than PGA-AG, and these results support the above hypothesis that pore shrinkage and pore rotation are competing effects, and the amount of each observed depends on the strength and stiffness of the material.

### 4.8.4 Pore Angularity

The shape of a particle is often described in terms of three parameters: form (or roundness), texture and angularity [66,67]. Form defines the bulk shape of the material, disregarding smaller details in the shape of the particle. Texture is used to define small-scale deviations from the bulk behaviour defined by form. Angularity covers length scales between those defined by form and texture [68]. Figure 4.35 shows a schematic of a particle with a comparison of the size ranges that form, texture and angularity measurements are based upon.
All of the analyses performed so far – calculation of pore area, eccentricity and orientation – are governed by behaviour at the bulk pore level, like form as shown in Figure 4.35. This makes measurements of angularity and texture more novel. However, due to the limited resolution of the data available it was decided that studying texture would be difficult. Small scale features may not be well resolved and will create large associated errors. Therefore it was decided that a study of pore angularity would fulfil the desire to have more precise data on the shape of pores, without having data that is dominated by associated errors.

4.8.4.1 Calculation of Pore Angularity

Angularity does not have a single definition, or a single accepted method of calculation. Different fields define different measures of angularity and use different experimental techniques to calculate them. For example, one of the older techniques is to compare the particles being studied with standardised silhouette charts [69]. This is purely a qualitative technique and is highly subjective.

Quantification of angularity was made significantly more feasible with the advent of quantitative image analysis techniques. A more modern technique that takes advantage of this involves quantifying the diameter of each corner (defined by fitting a circle to each corner of the particle), finding the average of this value, and weighting the result by the largest circle that can fit inside the particle [69]. Angularity can also be
quantified as the difference between the radius of a particle in a specific direction and the radius of a fitted ellipse in the same direction [67]. An ellipse is fitted to a particle, with the ellipse having the same centroid, area and aspect ratio as the particle itself, as discussed in Section 4.8.2. The ellipse has zero angularity. Hence the sum of differences in radius between the ellipse and the particle at all angles can be used as a measure of angularity, $A_n$, as shown in Equation (4.19) [67]:

$$A_n = \sum_{\theta=0}^{\theta=359} \frac{|R_{p\theta} - R_{E\theta}|}{R_{E\theta}}$$  

(4.19)

where $R_{p\theta}$ is the radius of the particle at angle $\theta$, and $R_{E\theta}$ is the radius of the fitted ellipse at angle $\theta$.

None of these existing methods of quantifying angularity were deemed suitable based upon the data and analytical software available. Therefore, a new method to determine a measure of angularity was proposed. The technique is a modified form of the radius-based method shown in Equation (4.19).

During the pore eccentricity study discussed in Section 4.8.2, ellipses are fitted to each individual pore in order to approximate the eccentricities of the pores. A novel method was proposed to determine whether a pore could be reasonably described by a fitted ellipse, since some morphologically complex pores were not being fitted with accurate ellipses. The method involved calculating the perimeter of each pore and its associated ellipsoid, and taking the ratio of the two values. Since the ratio for a perfect fitting ellipse would be 1, deviation from this value is indicative of a poorly fitting ellipse.

An ellipse has an angularity of zero, so it is proposed that a similar technique can be used to calculate a measure of angularity for each pore. Once again the perimeter of each pore and its associated ellipse are calculated. Deviation in pore shape from the ellipse is indicative of surface roughness, and since the fitted ellipse always has the same centroid location and aspect ratio of the pore itself, it is reasonable to assume that the greater the difference in perimeters of the pore and the ellipse, the more angular the pore. To quantify the behaviour of the bulk sample, the average value across all pores in a sample can be determined.
The main sources of error for these calculations are the error due to thresholding, discussed in Section 4.7, and the error due to pixel size. The error due to pixel size is calculated in terms of the semi-major and semi-minor axes as defined in Equation (4.7).

Expanding Equation (4.7):

\[
p = 3\pi a + 3\pi b - \sqrt{3a^2 + 3b^2 + 10ab}
\]  
(4.20)

The three discrete terms in Equation (4.20) can be defined as new variables \( X \), \( Y \) and \( Z \) respectively. Hence the error associated with the pore perimeter, \( p \), is:

\[
(\sigma_p)^2 = (\sigma_X)^2 + (\sigma_Y)^2 + (\sigma_Z)^2
\]  
(4.21)

The errors on \( X \) and \( Y \) are simple to calculate:

\[
\sigma_X = 3\pi \sigma_a
\]  
(4.22)

\[
\sigma_Y = 3\pi \sigma_b
\]  
(4.23)

The error on \( Z \) is more complex, and can be calculated by introducing a new variable \( D \), where:

\[
Z = \pi \sqrt{3a^2 + 3b^2 + 10ab} = \pi D^{1/2}
\]  
(4.24)

\[
D = 3a^2 + 3b^2 + 10ab
\]  
(4.25)

The error on \( D \) is defined as:

\[
\sigma_Z = \frac{\pi \sigma_D}{2D}Z
\]  
(4.26)
where:

\[
\sigma_D = \sqrt{(18a\sigma_a)^2 + (18b\sigma_b)^2 + \left(100ab\sqrt{\frac{\sigma_a}{a} + \frac{\sigma_b}{b}}\right)^2}
\]  \hspace{1cm} (4.27)

Through study of experimental data, it was found that \(\sigma_z << \sigma_x\) and \(\sigma_z << \sigma_y\). Therefore, Equation (4.21) can be approximated as:

\[
(\sigma_p)^2 \approx (\sigma_x)^2 + (\sigma_y)^2
\]  \hspace{1cm} (4.28)

\[
(\sigma_p)^2 \approx (3\pi\sigma_a)^2 + (3\pi\sigma_b)^2
\]  \hspace{1cm} (4.29)

\[
\sigma_p \approx \sqrt{(3\pi\sigma_a)^2 + (3\pi\sigma_b)^2}
\]  \hspace{1cm} (4.30)

The error associated with pixel size calculated using Equation (4.30) was combined in quadrature with the error due to thresholding to determine the total error on the pore perimeter values.

Figure 4.36 shows the rate of change of mean measure of angularity with increasing stress for pores in each of the three samples studied.
Figure 4.36: Rate of change of the measure of angularity with increasing stress for Gilsocarbon and PGA samples.

The mean measure of angularity for Gilsocarbon exhibited very little change during the application of a compressive load. Applying a linear best-fitting line suggests that there is a small downward trend, but due to the size of the errors associated with the Gilsocarbon data, the observed downward trend may not be statistically significant. Gilsocarbon has the highest stiffness out of the three samples by a large margin, and previous studies into variation of pore area and eccentricity have consistently demonstrated that Gilsocarbon experiences the smallest changes due to compressive loading of three samples.

The observed behaviour suggests one of two things is happening to the pores – they were not deforming, thus the mean measure of angularity remains largely unchanged; or the pores were deforming in such a way that angularity was not significantly affected. Studies of pore areas clearly show that the pores were deforming, which makes the latter theory more probable. It is known that materials of high stiffness shrink less when loaded, as discussed in Section 4.8.1. Therefore, the small change in angularity is expected to be predominantly explained by the stiffness of the material.
The small reduction of the mean measure of angularity suggests that the pores were becoming smoother and more uniformly shaped. Gilsocarbon is manufactured to be semi-isotropic, with no preferential orientation of filler particles. However, Figure 4.32 shows that there is a small degree of preferential ordering at an angle of approximately 25°, measured anticlockwise from the loading axis. This ordering of pores is similar to that observed in the PGA-WG sample, albeit much weaker. Therefore if pore orientation has an effect on the measure of pore angularity in graphite, similar behaviour would be expected in Gilsocarbon and PGA-WG, and the PGA-AG sample should exhibit different behaviour to Gilsocarbon and PGA-WG.

By comparison, the two PGA samples exhibit a greater degree of variation of the mean measure of angularity. The rate of change for the PGA-AG sample is approximately twice that of the PGA-WG sample. PGA-AG has been shown to be more susceptible to loading-induced deformation than PGA-WG due to its lower stiffness. It was expected that the PGA-AG sample would exhibit greater changes in the measure of angularity than the PGA-WG sample, but it was not initially clear what the exact nature of these changes would be.

The most notable result shown in Figure 4.36 was that the PGA-AG sample underwent an increase in mean measure of angularity, while the PGA-WG experienced a decrease in mean measure of angularity. Since the two samples are comprised of the same material and the only major difference between them is the orientation of the extrusion direction, it is likely that the orientation of filler particles, and hence the pores within the filler particles, govern the behaviour of pore angularity. This theory is corroborated by the observation that Gilsocarbon and PGA-WG, materials with alignment along the loading axis (albeit weak alignment in Gilsocarbon’s case), both exhibited a reduction in mean measure of angularity; while PGA-AG with the opposite orientation exhibited an increase in angularity.

These observations suggest that highly eccentric pores oriented parallel to the loading axis, as observed in PGA-WG and to a lesser extent Gilsocarbon, become less angular during the application of an axial load. This means the sample becomes smoother and more regular. Conversely, pores oriented perpendicular to the loading axis become more angular and less smooth when stressed.
4.8.5 Pore Separation Analysis

‘Pore separation’ refers to the spacing between pores, therefore an analysis of pore separation can also be considered as a study of localised strains. There is no fixed definition for pore separation and there are many different techniques for quantifying measures of pore separation.

It is difficult to analyse changes specifically occurring within the binder and filler phases of graphite. While the pores can be segmented and defined easily, the non-pore regions are continuous, meaning they cannot be segmented using the techniques already established. A number of methodologies of continuous region analysis were studied and attempts were made to apply them to the data collected, but it no technique was found that could completely eliminate deformation of pore regions whilst analysing deformation of the binder and filler phases.

However, two distinct methods were selected that can be used to focus on the behaviour of the non-pore regions by minimising the effects of the pore regions. Each method contained at least one flaw or drawback that the other method could take into account. Therefore, two separate methodologies for quantifying stress-induced pore separation behaviour were utilised. By using two techniques the drawbacks associated with each were eliminated.

The first method involved calculating ‘nearest neighbour’ distances. This refers to the shortest distance between each pore and the nearest separate pore. By determining the nearest neighbour distance for every pore at a series of applied loads, it is possible to quantify the contraction occurring in the binder and filler regions. Combining this data with the contraction of open pores observed in Section 4.8.1, all phases of the graphite samples can be considered and a full understanding of how the material responds to stresses can be gained.

A ‘nearest neighbour analysis’ plugin in the Fiji software [64] which calculates the shortest linear distance between features of interest, in this case the pores, was used for this analysis. The thresholded images were binarised such that the only features remaining in the images were the segmented pores, as required by the plugin. The plugin subsequently determined the co-ordinates of each pore and calculated the shortest distance from the centroid of each pore to its nearest neighbour.
This method allows quantification of pore separation, but does not give any information on the directions or angles of the pairs of pores with respect to the loading axis. Certain results may be of limited use, for example if the shortest distance between two pores is perpendicular to the loading direction, studying the variation of this value during loading will give little insight into the sample’s deformation behaviour. The other flaw with this technique is that the pores are defined using their centroids, and distances between pores are measured between centroids. The technique would be more useful if the distances were calculated between the edges of each pore, so that the distances being calculated are purely in the binder and filler phases of the material.

The second method of studying changes to pore separation attempts to address the issues with the nearest neighbour analysis technique by performing a Voronoi analysis. Voronoi analysis gives proximity information about a series of objects in an image by enclosing each object in a discrete cell, the size of which is defined so that at any point in the cell the enclosed object is always the nearest object. By thresholding the images and specifying the open pores as the objects of interest, Voronoi diagrams were produced and the area of each Voronoi cell calculated. By subtracting the pore areas from the Voronoi cell areas, the deformation of the non-pore regions can be isolated to a reasonable degree of accuracy. Changes to the sizes of the cells were studied during loading to determine how the proximity of the pores changes, i.e. the deformation of the binder and filler phases. An example of this technique is shown in Figure 4.37.
This method gives full two dimensional information on changes to pore separation distances, making it more useful than the ‘nearest neighbour’ analysis. The Voronoi cells are also calculated using the full extent of pores, as opposed to just the centroids, meaning that the technique is better suited for quantification of deformation in binder and filler regions. However, when analysing the data and attempting to quantify pore separation, the area data from this analysis is more difficult to physically interpret than the Euclidian distance calculations from the nearest neighbour analysis.

Both the nearest neighbour and Voronoi techniques have advantages and drawbacks when trying to quantify the stress-induced closure of non-pore regions. By using both methods to offset each other’s flaws, it was hoped that an understanding of variation of pore separation could be gained.

### 4.8.5.1 Nearest Neighbour Analysis

Pore separation during loading was first quantified by calculating distances between the centroids of individual pores and their ‘nearest neighbours’ using a suitable plugin in the Fiji software designed by Mao [70]. The variation of mean nearest neighbour distances with increasing applied load is shown in Figure 4.38 and Figure 4.39.

![Figure 4.37: Images showing a segmented and binarised region of a Gilsocarbon sample (left) and the Voronoi diagram for this region (right).](image)
In both PGA and Gilsocharbon, the mean nearest neighbour distances are significantly smaller than the mean pore diameters. This suggests that pore regions make up a much greater area of the sample’s surfaces than non-pore regions. This is disproved through observation of images of the material, such as those in Figure 4.17.
The reason for these seemingly conflicting observations is the dominance of small pores in the sample. Figure 4.22 shows the significant bias towards small pores, and the smallest resolvable pores in the images in Figure 4.17 are of a similar size the mean nearest neighbour distances shown in Figure 4.39. Since the smallest pores are great in number, they have a significant effect upon mean pore sizes. Therefore, the fact that spacing between pores is smaller than mean pore sizes does not imply that the material is dominated by porosity.

In Gilsocarbon, compressing the sample resulted in a linear decrease in mean ‘nearest neighbour’ distances from 54.05 µm to 53.55 µm. This shows that as well as the pore closure discussed in Section 4.1, the filler particles and binder phase are also collapsing and contributing to the shrinkage of the sample. At loads approaching failure, pores are known to open and grow in the filler particles in Gilsocarbon. Thus a greater than average decrease in pore separation distances was expected at the highest loads. There is not sufficient evidence to conclusively determine whether or not this has occurred.

Similar behaviour was observed in the PGA samples. Inter-pore distances are much smaller in the PGA samples than in the Gilsocarbon samples because PGA has approximately twice as many pores per unit area than Gilsocarbon. More contraction per unit applied stress was observed in PGA than in Gilsocarbon due to PGA’s lower compressive strength in each direction. In the both PGA samples, a linear decrease in mean pore nearest neighbour distances was observed. The rate of change was greater in the sample loaded perpendicular to the grain direction.

A number of separate mechanisms combine to explain the observed behaviour. As the samples were compressed, in each case the contraction in the loading axis reduces the distance between pores at most loads. Conversely, sample expansion in directions orthogonal to the loading axis will increase the intra-pore distance in these directions: a Poisson’s effect. Magnitude of expansion perpendicular to the loading axis due to the sample flexing was expected to vary, depending on how close to the centre of the sample the region of interest is. Gilsocarbon is known to have a Poisson’s ratio of 0.21, while PGA has Poisson’s ratios of 0.07 respectively both with and against the grain [17], and sample expansion in the orthogonal directions has been observed to be small in comparison to contraction in the loading direction. Hence contraction along the
loading axis was expected to dominate, and study of nearest neighbour distances is believed to be a useful technique for study of contraction of non-pore regions.

4.8.5.2 Voronoi Analysis

As discussed in Section 4.8.5, Voronoi analysis can allow a different way of studying deformation of the non-pore regions of the graphite samples. Figure 4.40 and Figure 4.41 show the variation of mean Voronoi cell areas samples of Gilsocarbon and PGA respectively during the application of an axial compressing load.

Figure 4.40: Variation of mean Voronoi cell size for a Gilsocarbon sample during the application of an axial compressive load.
Figure 4.41: Variation of mean Voronoi cell size for a PGA sample during the application of an axial compressive load.

The above graphs show the mean Voronoi cell areas. These areas include the pores themselves, which must be eliminated in order to exclusively quantify deformation of the binder and filler regions. Therefore, the area of each pore was subtracted from the area of the Voronoi cell enclosing it in order to quantify the Voronoi cell areas that were comprised of non-pore phases, i.e. binder and filler materials.
In Gilsocarbon, the mean cell size decreased as the load increased, as expected. The relationship between cell area and applied stress is inversely linear, which suggests that compression of non-pore regions occurs at a continuous rate. Mean cell sizes in
the PGA samples were around 30% smaller than in Gilsocarbon, which was expected since PGA is known to have a greater number of pores per unit volume than Gilsocarbon. In both PGA-WG and PGA-AG samples the mean cell size was found to decrease linearly as the applied load was increased. This suggests that contraction of the filler particles and binder matrix occurs at a continuous rate as the load increases. There was no evidence of the rate of contraction slowing down as the sample approached failure, as observed in the Gilsocarbon sample.

The rate of decrease was greater in PGA-AG than in PGA-WG. This suggests that the binder or the filler regions of the material exhibited a preferred orientation similar to that observed in the pore structure, and that this preferred orientation is stronger when aligned in the loading direction. If this were not the case, it is expected that the PGA-AG and PGA-WG samples would exhibit similar trends. Since the pore size changes have been removed, the changes in Figure 4.42 and Figure 4.43 are solely due to the binder and filler phases. Rotation of the sample through 90° is sufficient to cause changes in the rate of sample shrinkage. Through observation of microscopy images, the binder phase was found to have no preferential orientation, so the difference in behaviour is believed to be due to the orientation of the filler particles, which has been shown to gain preferential alignment during the extrusion aspect of the manufacturing process.

4.9 Conclusions

The confocal microscopy experiments have yielded valuable insight into the stress-induced deformation behaviour of open pores at the surface of the graphite samples. By considering the variation of a number of different pore shape, size and distribution parameters such as areas, orientation and eccentricity, significant information regarding the behaviour of porosity in graphite when exposed to stresses has been gained.

In both PGA and Gilsocarbon a strong bias towards small pores were observed. As pore area increased, the frequency of the pores decreased by a power law. However, smaller pores have less of an overall effect on the behaviour of the bulk material than larger pores. Hence the overall effects of the pore structure on the bulk
properties of graphite are a combination of relatively small effects of a large number of small pores, and relatively large effects from a small number of large pores.

At low loads, the deformation caused by compressive loading was observed to manifest itself predominantly through closure of pores and cracks, with a smaller component caused by collapse of filler particles and the binder region. As the graphite samples were compressed close to failure, however, more significant changes to the microstructure were observed; these changes were attributed to the growth and extension of pores in the filler particles and the filler particles’ subsequent collapse. The amount of pore closure in each sample during application of compressive loads was as expected based upon the values of compressive stress defined in Table 1.4. A major cause of these variations was found to be the morphology of the open pore structure.

Compressive loading was found to deform pores differently depending on their shape and orientation. This was most apparent in the PGA samples whose long, thin, preferentially ordered pores exhibited differing amounts of deformation and had different effects on the overall strength of the material depending on their orientation with respect to the applied load. The Gilsocarbon samples, manufactured to be quasi-isotropic, were found to have a slight preference in pore orientation in one direction. In PGA graphite the filler particles and the pores enclosed within them were found to be the dominant cause of variation of stress-induced damage in different directions, due to their long thin shape and preferential orientation. By comparison, the behaviour of the binder phase and the pores enclosed within it, although still affected by loading stresses, was more isotropic. Following the study of loading-induced variation of pore orientation, it was proposed that pore rotation and pore collapse were competing behaviours, but were not mutually exclusive. Grades of graphite with a lower compressive strength saw their pores exhibit greater contraction and less rotation than those with a higher compressive strength. However, in each case the pores rotated clockwise and the mean amount of rotation was very small.

These results emphasise the complex relationships between the different ways that pore shape and size parameters are affected by stress. When stressed, each pore experiences a number of behaviours including collapse along the loading axis, possible expansion perpendicular to the loading axis and rotational effects. The deformation of the binder and filler phases that are in contact with the pores must also be considered.
By studying the behaviour of each parameter in turn, under the same set of loading conditions, a detailed understanding of the response of the pore structure to the build-up of stresses has been gained.

There are four main limitations to the experiments discussed in this chapter. The first limitation is the difficulty of accurately quantifying the behaviour of small pores due to the limited resolution of the microscope and the pixel size of the images. Pores in nuclear grade graphite exist on a range of length scales from millimetres down to Angstroms [18], and the pore area analyses have shown that pore frequency increases as pore size decreases. Acquiring higher resolution data will allow the observation and analysis of smaller pores. However, the reduction in strength of the material caused by the presence of pores decreases in magnitude as the pores in question become smaller, so it follows that the pores most important to the structural integrity of the samples are the larger pores, which have been included in this study.

The second limitation is due to the two-dimensional nature of the data. While the study of pore behaviour in two dimensions has yielded useful insight into the behaviour of the pore structure and its impact on the strength of the bulk material, the technique is limited to open pores near the surface of the samples. The methodologies and analyses discussed in this chapter have therefore been extended to three dimensions through the use of X-ray computed tomography. This technique enabled high resolution imaging of both the open pores at the surface and the closed pore structures in the interior of the sample, allowing further insight into the stress-induced deformation behaviour of nuclear grade graphite to be gained. These experiments are discussed in Chapter 5.

The third limitation is that studying the surfaces of the samples will not give a true depiction of the stresses that are present within the sample. It is known that during the application of an axial compressive load, the stresses that build up within the sample are non homogeneous. Instead, the stress distribution varies vary based upon the length and diameter of the sample [71], as shown in Figure 4.44.
Figure 4.44: Image showing the stress distribution within a sample compressed along the vertical plane. Contours represent relative intensity of stresses, and the shaded regions are the most severely stressed [71].

The compressive strength of a material can also be affected by the length to diameter ratio of the material. A study by Paterson and Wong [71] has showed that the compressive strength of a sample is constant above a length to diameter ratio of three, while decreasing the length to diameter ratio below three causes the compressive strength to increase. Due to the use of samples with length to diameter ratios of approximately one, it is likely that the measured compressive strengths of the samples discussed in this chapter were larger than their true compressive strengths.

The fourth limitation is due to the relatively small number of samples studied. All of the observations in this chapter have been made from the analysis of six graphite samples. However, the experimental and analytical techniques were designed to reduce and severity of the limited number of samples studied, and author believes that the observations presented in this chapter are both reliable and statistically significant. Although only a small number of samples were studied, each sample contained tens of thousands of pores that were observable through limited depth selectivity techniques. Since it is the behaviour of the pores that are of interest in the analyses in Sections 4.8.1 to 4.8.5, having tens of thousands of resolvable pores provided a suitable amount of data for these analyses. In addition, the study in Section 4.6 suggests that the sample sizes were large enough to be considered representative of the bulk material. The samples were large enough that they were not dominated by the effects of a small number of large microstructural features (such as filler particles or particularly large pores), and it is believed that further increases in sample size would not necessarily
result in a change to the mean values of pore properties presented in Sections 4.8.1 to 4.8.5.

The above observations suggest that the results presented in this chapter, although based upon a small number of samples, are derived from a large number of pores and from suitably large samples to be statistically significant. It is expected that further studies using new samples cut from the same blocks would yield similar results.

### 4.10 Summary

- A series of in-situ confocal microscopy experiments were performed during the application of axial compressive loads to determine how the pore structure varies during the build-up of stresses. Images were analysed in Fiji to acquire quantitative data regarding various properties of open pores.
- A series of preliminary cyclic loading experiments were performed. Basic stress-induced deformation behaviour was defined through the study of load-against-deformation graphs. These results were used to formalise the main confocal microscopy experimental programme.
- A novel technique was created to quantify the errors associated with the imprecise segmentation process.
- Stress-induced variation of pore areas was calculated. Mean pore areas were found to decrease linearly with increasing applied load. This behaviour was governed by the stiffness and preferential pore orientation of each grade of graphite, as well as due to the opening of new pores close to the failure load of the material.
- Variation of pore eccentricities was calculated by fitting ellipses to pores. A novel technique was created to identify poorly fitting ellipses, which were eliminated from the study. Pore eccentricity was observed to increase linearly as a load was applied. The rate of increase was governed by the stiffness of the material and the orientation of the pores with respect to the loading direction, particularly in the filler particles for PGA graphite.
- Pores were observed to rotate clockwise with respect to the loading axis during application of compressive loads. The inability to analyse rotation behaviour in
small pores was studied, and an unexpected degree of anisotropy was observed in the Gilsoarbon sample.

- A novel hypothesis for the results observed in the pore orientation study was proposed. This hypothesis proposes a conflict between pore orientation and pore rotation. A material that exhibits significant pore rotation when stressed is expected to exhibit less pore shrinkage, and vice versa.

- Existing methodologies for the study of particle angularity were adapted into a novel technique for measuring the angularity of pores. The measure of angularity was found to decrease linearly in materials with a degree of pore ordering parallel to the loading axis, and increase in materials with pores oriented perpendicular to the loading axis.

- Variation of particle spacing was measured by quantifying the distances between each pore and its ‘nearest neighbour’. Nearest neighbour distances were found to decrease linearly as the applied load increased. The rate of decrease was found to be governed by the Poisson ratio and the stiffness of the samples.

- Variation of particle spacing was also measured by quantifying the sizes of Voronoi cells defined for each particle. The mean Voronoi cell size decreased linearly with increasing applied load.

- The advantages and disadvantages of nearest neighbour and Voronoi methods for pore spacing analysis were discussed. Neither method was deemed inherently superior to the other, and the studies were found to complement each other well.
Chapter 5: X-Ray Computed Tomography Experiments

This chapter discusses a series of experiments performed using the second of three main experimental techniques selected for use for this project, X-ray computed tomography. The results of these experiments have been published in two conference papers, as discussed in Appendix A.

5.1 Introduction to X-Ray Computed Tomography

The data collected using the confocal microscope in Chapter 4 has yielded significant insight into the stress-induced deformation behaviour of graphite, but with very limited depth selectivity. Since stresses are generated throughout the entirety of graphite components during reactor operation, and not limited to the surface of the components, it is desirable to utilise three-dimensional techniques to assess internal as well as external changes to the material. A number of existing studies into the microstructure of graphite using three dimensional techniques were discussed in Chapter 2, and it was decided that X-ray tomography was the technique best suited for the study of the interior microstructure of graphite samples.

5.1.1 Theory of X-ray Tomography

X-ray tomography is a well established technique for the magnification and study of the interior structures of opaque materials. It makes use of the ability of high energy X-rays to penetrate through materials and undergo attenuation based upon the density of the material the radiation is travelling through.

Figure 5.1 shows a simplified schematic of an X-ray tomography scanner.
The object to be scanned is placed upon a stage that is capable of rotating through 360°. With the stage held stationary at a known orientation, X-rays are projected onto the sample. As the X-rays enter the sample, they are attenuated by the material they pass through. The denser the region, the more energy is expended by the X-rays as they travel through it. Therefore, for a material comprising regions of differing densities, X-rays passing through these regions will expend different amounts of energy, as defined by Equation (5.1):

\[
\frac{d\phi}{dz}(z) = -\mu' \varphi(z)
\]  

(5.1)

where \(\mu'\) is the attenuation coefficient of the material and \(\varphi(z)\) is the radiant flux at distance \(z\) through the material.

Once the X-rays have passed through the sample they hit a photomultiplier detector which converts the X-rays into a visible image, with the brightness of a region of the image proportional to the energy of the X-rays reaching that part of the detector. The result is a two dimensional image whose local brightness is an indicator of the density of the material the X-rays have travelled through. Dense regions will absorb a greater proportion of the X-rays, while less dense regions will absorb a smaller proportion of the X-rays. Hence bright regions of the image indicate high levels of transmission and dark regions indicate low levels of transmission.
A two dimensional image like this is of little use, but by combining a series of these images taken from different angles, it is possible to produce a three dimensional representation of the object. The sample is rotated slightly and the process is repeated, producing a sequence of two dimensional images each recorded at a slightly different angle. As the sample is rotated, hundreds of images are recorded. Once sufficient images have been collected, computer software can be used to reconstruct the images into a three dimensional object where the interior of the object has been fully resolved and can be studied in detail.

A considerable advantage of this technique is that it allows the study of the interior of materials without causing any damage to the graphite samples. The images produced can be very high quality, but rely on a large number of variables being fulfilled. These variables include:

- **Image resolution:** The resolution of the images are predominantly dependent on the distance between the X-ray source and the sample, the distance between the sample and the detector and the resolution of the detector. For a fixed source to detector distance, resolution can be maximised by minimising the distance from the source to the object. The parameter ‘geometric magnification’ can be defined as the ratio between the distance from the source to the detector and the distance from the object to the detector.

- **X-ray Energy:** The energy of the X-rays directly impacts the transmission rate through the sample. If the energy is too low the X-rays will be fully attenuated in the sample, but if the energy is too high the X-rays will pass through uninhibited, and it will not be possible to resolve the internal microstructure. Both of these scenarios will result in the production of unusable data.

- **Contrast:** Contrast refers to the difference between the background count and the number of counts being transmitted through the sample and reaching the detector. Both of these variables must be carefully controlled to ensure the internal structure of the sample can be observed. If the transmission rate is too low, too many X-rays are being fully attenuated, and the sample will appear opaque or very dark. If the transmission rate is too close to the background count, X-rays are passing through the sample with little attenuation. The sample will appear almost as bright as the background and little internal structure will be resolved.
• Filters: Filters placed between the source and the detector can be used to modify the X-ray energy spectrum by blocking specific parts of it, and are useful if the contrast in an image is not ideal. Applying a low energy filter will block low energy X-rays. Since the low energy X-rays would most likely be fully attenuated in the sample, applying the filter results in an increase in percentage transmission through the sample and possibly an improved contrast.

• Number of images: The more images that are recorded during the 360° rotation of the sample, the smaller the angle between each individual image. This means that the final image will be of higher quality.

• Sample size: The sample size has an effect on the resolution – the smaller the sample size, the smaller the required field of view is, and hence the attainable resolution is improved.

X-ray tomography is much more complicated than traditional microscopy or confocal laser microscopy, and has more limitations regarding what can successfully be scanned. However, the technique can provide data that is far superior and more applicable to real situations than data from two dimensional or ‘2.5 dimensional’ techniques.

5.2 Materials and Apparatus

5.2.1 The Tomography Scanner

The X-ray tomography experiments were performed using the Nikon Metrology 320/225 kV Custom Bay at the Manchester X-Ray Imaging Facility. This machine was selected due to the high resolution images attainable and its compatibility with in-situ sample environments. Figure 5.2 shows an image of the tomography scanner, while Table 5.1 shows the capabilities of the scanner.
Source | 225 kV multimetal, 320 kV tungsten  
Targets | Copper, molybdenum, silver, tungsten  
Resolution | 3 – 160 µm  
Typical scan times | 5 – 120 minutes  
Accepted sample diameter | 3 – 320 mm  
Accepted sample height | 3 – 800 mm  
Maximum load | 150 kg  

Table 5.1: Operational properties of the Nikon Metrology 320/225 kV Custom Bay.

5.2.2 The Axial Compression Rig

In order to apply an in-situ axial load to the samples, a compression rig manufactured by Deben was used, as shown in Figure 5.3. The rig consisted of a static base plate upon which the sample was mounted, with a moveable upper plate and a 5 kN load cell used to apply the compressive load. Integrated software allowed real-time control and tracking of the force applied to the sample to an accuracy of 0.1 N. Due to the size and shape of the loading rig, the distance from the X-ray source to the sample and the distance from the sample to the detector were quite large, causing limitations...
in the resolution of the images. The smallest possible pixel size attainable by the Custom Bay when the compression rig was in use was found to be 18.5 μm.

![Image](image.png)

Figure 5.3: The loading rig used in the X-ray tomography experiments and the laptop used to control the rig.

### 5.2.3 Samples and Sample Preparation

As discussed in Section 3.2.2, a series of cuboid samples were machined by the machining shop in the University of Manchester’s School of Mechanical, Aerospace and Civil Engineering. These samples were machined into cylinders of approximate height 10 mm and diameter 8 mm. The samples were polished using progressively finer grades of polishing paper, culminating with the use 2000 grit silicon carbide polishing pads. Impurities were removed by placing the sample in an ultrasonic bath containing acetone.

The properties of the samples used for the tomography experiments are shown in Table 5.2.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Material and Orientation</th>
<th>Cross-sectional area [mm²]</th>
<th>Compressive strength [MPa]</th>
<th>Failure load [kN]</th>
<th>Required loading cell [kN]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-006</td>
<td>Gilsocarbon</td>
<td>55.0</td>
<td>70</td>
<td>3.85</td>
<td>5</td>
</tr>
<tr>
<td>P-006</td>
<td>PGA - WG</td>
<td>51.2</td>
<td>27</td>
<td>1.38</td>
<td>5</td>
</tr>
<tr>
<td>P-106</td>
<td>PGA - AG</td>
<td>49.7</td>
<td>27</td>
<td>0.84</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5.2: Details on the three samples studied. Compressive strength values taken from Nightingale [10] and Bodel [46].

### 5.3 Imaging during Loading

After testing a range of scanning parameters, it was found that the optimal image quality could be achieved by using an applied voltage of 59 kV, a current of 323 µA and no filter. These settings produced images with transmission through the sample of approximately 20% and a background of approximately 55,000 counts. Using a monochromatic beam minimised the amount of beam hardening artefacts present in the reconstructed images. These parameters provided suitable contrast and transmission required for the study of the interior pore structures of the samples.

A series of axial compressive loads were applied to each sample. The samples were compressed to loads ranging between 0 N and 95% of the anticipated failure load of the sample, calculated using Equation 4.2 as defined in Section 4.3.

The initial scan for each sample was performed with a token non-zero force applied to the sample, to avoid the possibility of sample movement during initial contact between the sample and the loading ram. After this initial scan the compressive load applied to the sample was slowly increased. Periodically the sample was held at a constant load and allowed to settle for five minutes, after which a tomography scan was performed. Each full scan was comprised of 1500 projections across 360°, resulting in an image being recorded every 0.24° of rotation, and a full scan time of 36 minutes. This step size was a compromise between maximising the quality of the reconstructed images and the limited amount of time that the tomography scanner was available. In total, four scans were performed on each sample of PGA graphite, whilst five scans were performed on the Gilsocarbon sample. An
additional scan was performed on the Gilsocarbon sample due to having additional
time for one more scan after completing the first four scans on the three samples.

5.4 Data Reconstruction, Image Segmentation and
Segmentation Errors

The tomography data sets were reconstructed using the ASTRA toolbox created
by Palenstijn et al. [72] and HMtools, a collection of MATLAB functions maintained by
Dr R. Bradley of the Manchester X-ray Imaging Facility which assisted in the conversion
and reconstruction of the tomography data sets.

Initially, the 1500 individual images that would eventually comprise the three
dimensional reconstruction were read into the software. The centre of rotation, which
represents the points in a single image that underwent no translational movement
during rotation through 360°, was defined. Definition of the centre of rotation can be
performed using two techniques. The first technique is simply using appropriate
software to define it automatically. This technique is suitable for high contrast images
and images where the centre of rotation is well defined to begin with. This can be
accomplished by ensuring the sample is mounted as close as possible to the centre of
the rotation stage. The software has difficulties in defining the centre of rotation if
there is low contrast in the images or if the sample is not close to the centre of the
stage.

The second technique for determining the centre of rotation is defining it by
eye, using an iterative cycle of qualitative image studies. A single two-dimensional slice
is reconstructed from the tomography data with an estimation of the centre of
rotation. The centre of rotation can then be adjusted slightly and the new
reconstruction is compared to the initial reconstruction, to determine which is more
accurate. This process continues until the user is satisfied that an accurate centre of
rotation has been located. This technique is slower and requires user input, but is more
reliable than the automatic centre of rotation calculation method discussed above,
particularly for low contrast data. Although the data collected for this project is of
suitable contrast for both methods, it was decided that centres of rotation would be
determined manually to ensure the quality of the reconstructed images was as high as
possible.
After the centres of rotation were defined, the data were cropped to remove irrelevant regions of the images such as the sample stage or space surrounding the sample, and to reduce the file size. The images were then reconstructed into two file formats – a volume file (.vol) containing a three dimensional reconstruction of the whole image, and information about the volume file (.vgi) which, when combined, can be used to reconstruct the three dimensional image. The latter format is not commonly supported by many image analysis packages, so the `.vgi` files were converted to the more versatile *tagged image file format* (.tif). The `.tif` files are in the form of a series of two dimensional slices.

Once reconstructed, the images were imported into *Fiji* [64], an image analysis package that contains a number of programs and plugins that are particularly useful for tomography image analysis. Fiji is particularly suited for the quantitative analysis of tomography data because it is compatible with user-created plugins. The base software has significant capabilities for the analysis of three-dimensional data sets, and any gaps or flaws in the software were resolved through the use of user-created software.

To segment the pore structure in each sample and separate it from the binder and filler materials, a greyscale thresholding technique was used, similar to that used in the confocal laser microscopy experiments discussed in Chapter 4. A threshold intensity was defined such that voxels with an intensity below the threshold are defined as pores and voxels with an intensity greater than the threshold are not classed as pores. Although the resolution of the images were 18.5µm, it is not ideal to quantify pore properties at this level since small pores with sizes of the order of a few voxels will not be adequately resolved, and as such the error associated with each result will be significant. As the observed pores get larger, this source of error becomes less significant.

As discussed in Section 4.7, it is difficult to define the ideal greyscale value for the thresholding limit. There exists a range of values that could reasonably be defined as the thresholding limit, hence there is an error associated with any pores segmented using the thresholding technique. In order to calculate these errors, the same process was performed as for the confocal microscopy images.

A single tomography image was thresholded at a series of different greyscale brightness values, and the mean pore volume was calculated for each image. The greyscale curves for each sample are shown in Figure 5.4.
Both materials exhibit similar greyscale curves. In each case there is a narrow peak at low brightness. This peak corresponds to the regions where the X-rays are attenuated less when travelling towards the detector. The remainder of the spectrum represents the binder and filler regions. In the both images a second wider peak is present that represents the binder and filler phases.

For each image, an upper and lower limit was defined by eye for the region where the thresholding appears reasonable. The thresholding value directly in the middle of the upper and lower limit was then defined as the thresholding limit. The graphs used to calculate the errors for the Gilsocarbon and PGA samples are shown in Figure 5.5 and Figure 5.6 respectively.

Figure 5.5: Graph showing variation of mean pore area at different thresholding levels for Gilsocarbon graphite. The lower and upper bounds for reasonable thresholding were 22 and 28 respectively, resulting in a thresholding limit of 25 and errors of +6.52% and -11.11%. These errors are shown on the graph for each mean pore area value.
Figure 5.6: Graph showing variation of mean pore area at different thresholding levels for PGA graphite. The lower and upper bounds for reasonable thresholding were 13 and 17 respectively, resulting in a thresholding limit of 15 and errors of +5.80% and -4.69%. These errors are shown on the graph for each mean pore area value.

Using the error sizes calculated in Figure 5.5 and Figure 5.6, the errors due to thresholding introduced in any pore property calculations were calculated.

5.5 In-Situ X-Ray Tomography Images

For the Gilsocarbon sample, five images were recorded at a range of applied loads, while four images were collected for each PGA sample. Once the images were reconstructed, they were imported into two image analysis packages for study. The Fiji software that was used extensively for confocal microscopy data analysis can also be used for analysis of three-dimensional structures.

However, Fiji is less useful for visualising the sample in three dimensions in real time. The software displays the three-dimensional images as a stack of two-dimensional images, and allows the user to switch between layers at will. Although there are tools and plugins that allow data to be visualised in three dimensions, more appropriate software is available. For three-dimensional visualisation of data, it was decided that Avizo [73] software would be used. Avizo provides powerful tools for
viewing and manipulating data in three dimensions, and is much better suited for producing detailed images of the samples than Fiji.

However, Avizo contains significantly fewer quantitative analysis tools than Fiji. Therefore, it was decided that Fiji would be used for all of the quantitative analyses to be performed on the data, while Avizo would be used for qualitative analyses and to create high resolution, three-dimensional images of the samples.

The first set of images show three-dimensional representations of the three samples studied, with no in-situ load applied. These images were produced using Avizo. Figure 5.7 shows the Gilsocarbon sample while Figure 5.8 shows the PGA-AG and PGA-WG samples.

Figure 5.7: Three-dimensional representation of a Gilsocarbon sample acquired using X-ray tomography.
The tomography data were also analysed using Fiji. As discussed above, Fiji displays the data as a stack of two-dimensional slices. The slices can be analysed and manipulated individually or as a whole. Figure 5.9 and Figure 5.10 show images of a single slice of Gilsocharon, PGA-AG and PGA-WG, taken from the central layers of the samples. The interior pore structures of the samples can be seen clearly in images of individual slices.
The tomography data were quantitatively analysed in Fiji, using similar methods to those used in Section 4.8 to analyse the confocal laser microscopy data. The analytical software is capable of tracking properties across separate layers, so while Fiji
is not particularly effective at displaying data in three dimensions, it is capable of performing quantitative analyses in three dimensions. These analytical techniques were particularly useful for the analysis of the behaviour of the pore structure, discussed in Section 5.6.

5.6 Pore Dimensional and Property Analysis

Once the images were successfully segmented to define the pores, a series of quantitative analyses on each pore were performed to determine how the pores respond to the build-up of stresses.

Fiji contains a number of functions and tools which can be utilised to acquire numerical data from the confocal microscopy images and quantify a number of different pore properties. Many of the properties chosen for quantification were only possible to study by using three dimensional data, thus taking full advantage of the X-ray tomography technique. Some properties were also calculated using the confocal microscopy data, allowing a comparison between two- and three-dimensional techniques. The properties selected for study were:

- Pore volumes. Pore volumes represent the most suitable study of pore size behaviour, and can only be attained using three dimensional techniques such as X-ray tomography. It was expected that the results would represent a significant advance over the pore area data discussed in Section 4.8.1, and a detailed comparison of the two experimental processes was performed with the intention of determining how useful and relevant studies in fewer than three dimensions are when three-dimensional data is available.

- Pore eccentricities. Eccentricity is a measure of the degree that a three-dimensional object deviates from circularity. The ellipse fitting technique discussed in Section 4.8.2, and the novel technique used to determine the suitability of fitted ellipses, were extended to three dimensions, and a comparison of the results was performed.

- Pore surface areas. Pore surface areas can only be studied in three dimensions. This behaviour is important since the surface area of the pores defines the physical areas of the sample available for processes such as oxidation, where the greater the surface available for contact with gases in the reactor, the
higher the rate of oxidation. In addition, surface area to volume ratios were calculated and their importance for graphite moderator components was also discussed.

- Pore angularity. Angularity is a measure of how smooth the exterior edges of a feature are. The definition of angularity in Section 4.8.4 was extended to three dimensions, and a comparison was performed between the two data series.

The above properties were calculated for each pore observed in the images. The stress-induced deformation behaviour for each parameter is discussed in detail in Sections 5.6.1 to 5.6.4.

### 5.6.1 Pore Volumes

The volume of each individual pore was calculated with the assistance of the 3D Objects Counter plugin, a data analysis package created by Bolte and Cordelières [75] that quantifies multiple different parameters of objects defined through segmentation. In this case the plugin was used to calculate the volume of each individual pore. Pore volumes were calculated simply by calculating the number of discrete voxels that comprise each segmented region and multiplying that figure by the volume of a single voxel. Values of pore volumes were calculated for each sample at progressively higher loads to determine quantitatively how compressive stresses deform the pore structure.

Due to the presence of the large axial compression rig, the distance from the X-ray source to the sample and the distance from the sample to the detector were significant, which limited the effective resolution of the data. The resolution of each three dimensional reconstruction was 18.5 µm, which was significantly poorer than the 2.5 µm pixel size of the confocal microscopy data. This severely limited the ability to study small pores, which is problematic given that Figure 4.19 and Figure 4.20 exhibited a very strong bias towards small pores in the graphite samples.

As with the two dimensional data, a pore volume threshold was proposed, below which pores are considered too small to be accurately defined by the number of voxels available. A low threshold cut-off would minimise data loss and allow analysis of small pores, but at the expense of large errors associated with voxel size and potential difficulties with subsequent analyses (as evidenced by the problems with orientation.
analysis of small pores discussed in Section 4.8.3). A high threshold will result in the loss of a lot more data, but the remaining pores will be more accurately resolved.

It was decided that for pore volumes, applying a cutoff would result in the loss of too much data, particularly given the numbers of small pores present in the sample. Therefore no pore size cutoff was applied for the study of variation of pore volumes. Error analysis would emphasise the relatively large errors associated with the volumes of small pores.

There are two major sources of error that must be considered when calculating pore volumes. The first is the error due to thresholding, discussed in Section 5.4. The second error is due to voxel size. A methodology for calculating the error associated with pixel size for two dimensional data was discussed in Section 4.8.1, where an ellipse was fitted to each pore and the errors associated with the major and minor axes of the ellipse were used to estimate the error associated with the volume area of the pore. This technique was extended to three dimensions by fitting a three dimensional ellipsoid to each pore, the volume of which, \( V' \), is defined by:

\[
V' = \frac{4}{3} \pi abc
\]  

(5.2)

where \( a \), \( b \) and \( c \) are the lengths of the semi-principal axes of the ellipsoid.

Each voxel has a length of 18.5 \( \mu m \), so the error on each axis length is twice this value, as explained in Section 4.8.1. By combining the error on each axis in quadrature, the pore volume error due to voxel size, \( \sigma_A \), can be defined as:

\[
\sigma_A = \frac{4}{3} \pi \sqrt{\left(\frac{\sigma_a}{a}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_c}{c}\right)^2}
\]  

(5.3)

Figure 5.11 shows the range of pore volumes observed in the Gilsocarbon sample, while Figure 5.12 shows the range of pore volumes observed in the PGA samples, with no applied load. In each case pores up to a size of 0.0029 mm\(^3\) are shown. Although there are some pores with volumes exceeding the range shown in Figure 5.11 and Figure 5.12, they contribute less than 0.1% of the total number of pores observed in the Gilsocarbon and PGA samples.
Figure 5.11: Distribution of the range of pore volumes present in the Gilsocarbon sample with a token external load applied. A logarithmic y-axis is used to increase readability of data. The observed relationship is well described by a power law.

Figure 5.12: Distribution of the range of pore volumes present in the PGA samples with a token external load applied. A logarithmic y-axis is used to increase readability of data. The observed relationships are well described by power laws.
The bias towards small pores is just as clear in the three dimensional data as in the two dimensional data presented in Section 4.8.1, despite the fact that the ability to resolve small pores in the three dimensional data is limited by larger voxel sizes.

Both PGA and Gilsocarbon grades of graphite were observed to exhibit broadly similar pore size distributions. A power law of the form \( f = A v^B \), where \( f \) is the observed frequency of pores of volume \( v \), and \( A \) and \( B \) are constants, described the relationship between pore size and frequency well. To aid comparison between the three data series, the data have been plotted on log-log axes in Figure 5.13, which has the effect of making data that obeys a power law appear linear. In each case the exponent of the \( f = A v^B \) relationship is the gradient of the best-fitting line when plotted on log-log axes. As discussed in Section 4.8.1, the pore size distribution can be analysed as a fractal distribution using Equation (4.5).

![Figure 5.13: Pore volume distributions for Gilsocarbon and PGA graphite samples, plotted on logarithmic axes. A power law has been fitted to each data series.](image)

Additional pore volume data was collected during the application of progressively greater compressive loads upon each sample. Figure 5.14 shows the mean pore volume at each level of applied load for the three samples of graphite.
studied. The applied loads are quantified as ratios to the materials’ anticipated failure load calculated using Equation 4.2. At low volumes the accuracy of the data was limited by the resolution of the image, hence, as sample size increases, the contribution of pixel size to the total error becomes smaller.

Figure 5.14: Mean pore volumes at a range of applied loads for each graphite sample. Stresses are shown as a ratio to the expected failure load of the sample calculated using Equation 4.2 and data from Table 5.2. Quadratic best-fitting curves are shown for each sample.

In each case the mean pore volume decreased as the applied load increased. This was expected since during the application of the compressive load, the bulk volume of the sample decreased, and it is easier for pores to accommodate this sample contraction by collapsing than for the binder or filler phases to contract.

The observed changes in mean pore volume were relatively small in Gilsocarbon compared to the PGA-AG sample, which was expected since the stiffness of Gilsocarbon is greater than that of PGA-AG graphite. However, the rate of change of pore volumes in Gilsocarbon was very similar to that of the PGA-WG sample, despite the differences in stiffness for the two materials.

Furthermore, the rate of volume change in the PGA sample loaded parallel to the grain direction (PGA-WG) was smaller than that observed in the sample loaded
perpendicular to the grain direction (PGA-AG). This behaviour is explained by the filler phase of the materials. The long thin filler particles in PGA graphite become oriented along the grain direction during manufacturing. As discussed in Section 4.8.2 and in Figure 4.26, these particles are much more resistant to shrinkage when compressed parallel to their long axis than when compressed perpendicular to the long axis, therefore the stiffness of the filler particles (and hence the bulk material) is greater in the grain direction. The filler phase in Gilsocarbon consists of spherical filler particles with no preferential directionality. Pores appear to be distributed evenly in all directions in both the filler phase and the binder phase, so the pores have a much smaller effect on the overall resistance to deformation of Gilsocarbon than in PGA.

For the PGA-AG sample, a quadratic fit appears to describe the data well. For the Gilsocarbon and PGA-WG samples, however, it was not clear whether a linear fit or a quadratic fit best describes the data in Figure 5.14. To determine the most suitable fit, a linear regression analysis technique involving the calculation of $R^2$ statistics, measures of goodness of fit, was used. An $R^2$ value for a best fitting curve calculates how close the data points are to the curve. Table 5.3 shows the calculated $R^2$ values using both linear and quadratic fitting techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R^2$ – linear</th>
<th>$R^2$ – quadratic</th>
<th>Appropriate fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gilsocarbon</td>
<td>0.9877</td>
<td>0.9976</td>
<td>Quadratic curve</td>
</tr>
<tr>
<td>PGA-AG</td>
<td>0.9110</td>
<td>0.9991</td>
<td>Quadratic curve</td>
</tr>
<tr>
<td>PGA-WG</td>
<td>0.9889</td>
<td>0.9987</td>
<td>Quadratic curve</td>
</tr>
</tbody>
</table>

Table 5.3: A comparison of linear and quadratic fits for each graphite sample, with goodness of fit quantifies using linear regression analysis.

The results in Table 5.3 show that both linear and quadratic curves fit the data very well, since high $R^2$ values are typically an indication of a good fit. However, in each case the $R^2$ values for the quadratic curve are higher than those for the corresponding linear fits, meaning the quadratic fitting curve is most suitable for each of the three samples. This was confirmed by studying the residuals for each data point, as shown in Figure 5.15. Residuals are defined as the difference between the actual value of a data point and the value expected from the fitting curve. There are situations where a high
$R^2$ value may not be indicative of a good fit (such as data containing an inherent bias), and studying the residuals can confirm this.

If a graph of residuals shows any clear patterns or trend, the fit may be flawed in some way [76]. For example, it could suggest that there is an inherent bias in the best fitting line, or that the line consistently over-predicts or under-predicts aspects of the observed properties. Since the data in Figure 5.15 shows no pattern, it suggests that the choice of a quadratic fit for the data in Figure 5.14 is suitable.

In both Gilsocarbon and PGA, mean pore volumes appear to decrease quadratically, which suggests that the rate at which pores collapse and close increases as the applied load increases. The quadratic relationship was unexpected since the study performed using two-dimensional pore area data in Section 4.8.1 showed a linear relationship between mean pore area and applied load. Table 5.3 shows that although the data are best described by a quadratic fit, a linear fit still provides a reasonable approximation of the reduction in mean pore volume. Since pore area and pore volume are both parameters that define pore size, it was anticipated that both variables would exhibit similar behaviour when the samples were compressed, but this does not appear to be the case. This unexpected outcome is discussed in detail in Section 5.6.1.1.
5.6.1.1 Comparison to Confocal Laser Microscopy Data

The observed changes in pore volume using X-ray tomography were compared to the equivalent observations of pore areas from the confocal microscopy experiments.

Looking at the histograms of pore areas and pore volumes shown in Figure 4.22 and Figure 5.13 respectively, both techniques exhibit a power law relationship between a specific pore size and the frequency of pores of this size within the material. The power term in each best-fitting line ranged from -1.68 to -2.21 for pore areas and -1.96 to -2.32 for pore volumes, which shows a surprising degree of consistency between the results. This was unexpected since pore areas and volumes are different parameters, despite the fact that are both measures of pore size.

Since the samples for each set of experiments were different sizes and were exposed to different amounts of loading, it is difficult to compare the two sets of absolute data values. Instead, relative values were used when comparing the mean pore areas and volumes.

Figure 5.16 shows the data from Figure 4.22 and Figure 5.14 plotted in a different manner so that they can be compared with one another. The x-axis shows the applied load as a ratio to the failure load, which means that samples loaded to significantly different levels of stress can be compared easily. The y-axis shows the mean pore area to volume as a ratio to the mean pore area to volume at zero load. A linear fit has been applied to the tomography data. Although this fit is not as suitable as the quadratic fit shown in Figure 5.14, it still has a very high $R^2$ statistic, as shown in Table 5.3. The advantage of using a linear fit is that the gradients of the lines, here representing the rate of change of pore volume with increasing stress, can be easily compared to the linear fits applied to the two dimensional data.
Comparing the two sets of data in Figure 5.16, very similar behaviour is observed for the pore volume and pore area variation. For each confocal microscopy technique, the closure of pores in the Gilsocarbon and PGA-AG samples occur at a similar rate, despite the compressive strength of the Gilsocarbon sample being significantly greater than that of the PGA-AG sample. This behaviour is also observed for Gilsocarbon and PGA-AG analysed using X-ray tomography. For both techniques, the rate of change of pore sizes for the PGA-WG sample is much lower than for PGA-AG and Gilsocarbon.

It was expected that by displaying the data with respect to values that are independent of sample geometry, the tomography and confocal microscopy data would follow similar trends. Since pore areas and pore volumes are both parameters that define the size of pores, it seemed reasonable to expect that the behaviour of the two parameters would be similar, or related to one another by a simple mathematical relationship. However, the rate of change of pore volumes is significantly lower than the rate of change of pore areas for each sample. Table 5.4 shows that the tomography analyses and confocal microscopy analyses of stress-induced contraction for each
sample are remarkably consistent. Pore volumes for each grade of graphite decreased by a factor of approximately four times less than pore areas, per unit stress.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate of change – pore areas</th>
<th>Rate of change – pore volumes</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gilsocarbon</td>
<td>-0.26500</td>
<td>-0.06008</td>
<td>4.41078</td>
</tr>
<tr>
<td>PGA-AG</td>
<td>-0.31275</td>
<td>-0.07907</td>
<td>3.95536</td>
</tr>
<tr>
<td>PGA-WG</td>
<td>-0.14076</td>
<td>-0.03458</td>
<td>4.07056</td>
</tr>
</tbody>
</table>

Table 5.4: The rate of change of pore areas and pore volumes due to growth of stresses, and the ratio between these variables.

The consistency of this behaviour suggests that it occurs as a result of the difference between the way two dimensional data and three dimensional data are visualised and interpreted; and not as a result of differences between the microstructures of the samples.

This hypothesis can be tested by performing a two-dimensional analysis on a single slice of the tomography data. By performing an analysis of pore areas (or pore cross-sectional areas if the slices being studied are in the interior of the samples), the results can be compared to the pore areas calculated using confocal microscopy. If the observed behaviours are similar, this would suggest that the unexpected results observed in Figure 5.16 are due to the differences in methods of interpreting two-dimensional and three-dimensional data.

Five slices from the Gilsocarbon tomography data were selected for further study – the top slice, the bottom slice and three slices from the interior. The mean pore areas were calculated for each slice at each level of applied load, and the results are shown in Figure 5.17.
The loading-induced pore contraction observed in Figure 5.17 exhibit linear behaviour, similar to the data achieved through confocal microscopy shown in Figure 4.22. This suggests that the observed variation of pore areas and pore volumes are independent of the data acquisition techniques employed by the author, and depend solely on the differences in two- and three-dimensional data. More importantly, it shows that there are significant differences between the outcomes of two-dimensional studies and three-dimensional studies of similar parameters. However, different characterisation techniques may give different pore area or volume values, which may result in a different relationship between the results being observed. It is anticipated though that the relationship between the two sets of results will still be linear, as it was in Table 5.4.

Although the trends observed in Figure 5.17 are consistent and are independent of the location of the slice within the sample, the actual values of mean pore entrance area do appear to vary depending on the location of the slice. This is not surprising, since, as shown in Figure 4.44, the stress distribution within each sample is not homogeneous. The data in Figure 5.17 suggest that as the region being considered moves down through the sample, the mean pore area decreases until the centre of the

Figure 5.17: Variation in mean pore areas for five slices through the Gilsocarbon sample.
sample is reached, after which the mean pore area increases again. Figure 4.44 suggests that the largest stress concentrations are present within the central slices of the sample, which supports the results shown in Figure 5.17.

However, similar behaviour was not observed for all pore parameters that were studied. Pore orientation angles were studied within the five planes at different heights throughout the sample, and the results were consistent with one another. Overall, each slice exhibited a small amount of pore reorientation, and the height of the slice appeared to have no effect upon the amount of pore reorientation observed. Additional investigation of how inhomogeneous stress distributions affect behaviour at different heights within the samples may yield interesting insight into stress-induced dimensional change in graphite components, particularly for studies of full graphite bricks, as opposed to the small samples considered in this project.

Many two-dimensional studies have been performed into the behaviour of graphite, such as Bodel’s two-dimensional analysis of confocal microscopy data [46] and Kane’s quantitative analysis of pore behaviour from microscopy data [56]. In each case the observations have been made with the caveat that two-dimensional analyses of three-dimensional behaviours will not be truly indicative of the behaviour being studied. In many cases the analyses have been performed in two dimensions because three-dimensional techniques were not available, not feasible or not ideal for the experiments in question. The results of these experiments, while novel and insightful, were often limited in use compared to the equivalent results had they been recorded and analysed in three dimensions.

Through pore size analysis of both two-dimensional and three-dimensional data, as shown in Figure 5.16, the difference between pore area and pore volume measurements has been quantified. Pore volume measurements and pore area measurements were found to differ by a factor of approximately four. Further study is required to determine whether this trend continues across different materials, but confirmation of this behaviour would allow further insight to be gained from existing two-dimensional studies of graphite. It would also be interesting to compare two- and three-dimensional analytical techniques for other microstructural graphite parameters to determine how they correlate.
5.6.2 Pore Eccentricity

In Section 4.8.2 a technique for calculation of pore eccentricities was defined by fitting an ellipse to each pore and calculating the eccentricity, \( e \), of the pore in terms of its semi-major and semi-minor axes, \( a \) and \( b \) respectively, using Equation (4.5).

This technique was extended to the analysis of three-dimensional tomography data by fitting three dimensional ellipsoids to the data. An ellipsoid is the three-dimensional analogue of an ellipse, and has three axes which may be of differing lengths.

Eccentricities were calculated by fitting a three dimensional ellipsoid to each individual pore with the assistance of the 3D ImageJ Suite plugin created by Ollion et al. [74]. For each ellipsoid, values of the major radius (defined as half the length of the long axis of the ellipsoid), elongation (the ratio of major radius to the second radius) and flatness (the ratio of second radius to third radius) were calculated.

To simplify the eccentricity calculations, ellipsoids were defined with two of the axes having identical lengths, hence it is possible to define a semi-major axis, \( a \), and a two semi-minor axes, \( c \). To confirm the suitability of defining ellipsoids with identical length minor axes, the volume of each ellipsoid was calculated with three separate axis lengths and with identical minor axis lengths. The percentage difference between the two volume values for each pore was calculated, and it was found that 98% of the pairs of pore volumes differed by less than 1.7%. This suggested that the technique of fitting ellipsoids with identical minor axes to simplify eccentricity calculations was appropriate.

Ellipsoids can be defined as prolate or oblate, depending upon the axis about which the ellipsoid exhibits rotational symmetry. If an ellipsoid is symmetric when rotated about one of its minor axes, the ellipsoid is defined as being prolate. If an ellipsoid is symmetric when rotated about its major axis, the ellipsoid is defined as being oblate. This behaviour is shown in Figure 5.18.
Figure 5.18: Two distinct types of ellipsoid. Left: An oblate ellipsoid. Right: A prolate ellipsoid [77].

For prolate spheroids $a$ is greater than $c$. For oblate spheroids $c$ is greater than $a$. These properties were then used to calculate the eccentricity of each fitted ellipsoid, as defined by Equations (5.4) and (5.5):

\[
e^2 = 1 - (c^2 - a^2) \quad \text{for} \quad c < a
\]

(5.4)

\[
e^2 = 1 - (a^2 - c^2) \quad \text{for} \quad a < c
\]

(5.5)

The result is a value between 0 and 1, where 0 represents a perfect sphere and values approaching 1 indicate an increasingly elongated shape.

The ellipsoid-fitting technique experiences the same drawbacks that its two-dimensional equivalent does, most significantly the fact that it is not possible to fit an ellipsoid to certain irregularly shaped or structurally complex pores.

For the two dimensional data, a technique was created to identify pores which were badly defined by ellipses by comparing the perimeters of each pore and its fitted ellipse. It was proposed that perfect fitting ellipses would exhibit a pore perimeter to ellipse perimeter ratio of 1. Deviation from this value was indicative of a poorly fitting ellipse, and a cutoff was chosen beyond which pores were rejected from the study.

To extend this technique to three dimensions, a similar comparison was performed using the surface areas of pores and their fitted ellipsoids. As before, ratios of pore surface areas to fitted ellipsoid surface areas were calculated. An acceptable fitting range of $0.75 - 1.25$ was chosen through visual study of the data, and pores with
surface area ratios outside of this range were rejected from eccentricity calculations (resulting in rejection of approximately 18% of the pores).

The surface areas of the pores were calculated using the Fiji software, while the surface areas of the ellipsoids, $S$, were calculated in terms of their semi-axis lengths $a$, $b$ and $c$ using an equation defined by Thomsen [78]:

$$S \approx 4\pi \left( \frac{(ab)^p + (ac)^p + (bc)^p}{3} \right)^{1/p}$$  \hspace{2cm} (5.6)

where $p$ is a known constant. Currently $p = 1.6075$ is suggested for use due to it minimising the error (in the worst case ± 1.061 %) [78], but $p = 1.6$ has also been proposed, with the slightly greater error of ± 1.178 % in the worst case [79].

The main source of error associated with the eccentricity calculations is the error due to voxel size.

Considering Equation (5.4), a new variable $X$ is defined such that:

$$X = c^2a^{-2} \quad \therefore \quad e = (1 - X)^{1/2} \quad \text{for} \quad c < a$$ \hspace{2cm} (5.7)

$$X = a^2c^{-2} \quad \therefore \quad e = (1 - X)^{1/2} \quad \text{for} \quad a < c$$ \hspace{2cm} (5.8)

The error associated with $X$ can be defined as:

$$\sigma_X = X \sqrt{ \left( \frac{2\sigma_c}{c} \right)^2 + \left( \frac{-2\sigma_a}{a} \right)^2 } \quad \text{for} \quad c < a$$ \hspace{2cm} (5.9)

$$\sigma_X = X \sqrt{ \left( \frac{2\sigma_a}{a} \right)^2 + \left( \frac{-2\sigma_c}{c} \right)^2 } \quad \text{for} \quad a < c$$ \hspace{2cm} (5.10)

Equations (5.9) and (5.10) are identical since the negative term is removed during the squaring of each bracket. Therefore the error due to voxel size has no dependence on whether the fitted ellipsoid is oblate or prolate, as shown in Equation (5.11):
By combining Equations (5.7), (5.8) and (5.11) the error can be defined as:

\[
\frac{\sigma_e}{e} = \frac{1}{2} \left( 1 - \frac{X}{X} \right) \sigma_x \quad (5.12)
\]

\[
\sigma_e = \frac{e}{2} \frac{(1 - c^2a^{-2})}{\sqrt{\left(\frac{2\sigma_c}{c}\right)^2 + \left(\frac{2\sigma_a}{a}\right)^2}} \quad \text{for } c < a \quad (5.13)
\]

\[
\sigma_e = \frac{e}{2} \frac{(1 - a^2c^{-2})}{\sqrt{\left(\frac{2\sigma_c}{c}\right)^2 + \left(\frac{2\sigma_a}{a}\right)^2}} \quad \text{for } a < c \quad (5.14)
\]

Note that the dependence of Equation (5.12) on Equation (5.7) and Equation (5.8) reintroduces the dependence on whether the fitted ellipsoid is oblate or prolate on the overall error.

Pore eccentricities were initially studied with a token non-zero applied load. For each sample, the eccentricity of each pore that was well defined by an ellipsoid was calculated. The results were plotted in a histogram to show the frequency of pores observed at each degree of eccentricity, as shown in Figure 5.19.
Figure 5.19: The range of pore eccentricities observed in Gilscocarbon and PGA samples with zero applied load. An eccentricity of zero represents a perfect sphere, while progressively larger values indicate the pore has an increasingly large aspect ratio.

In all three cases the pore eccentricity distribution is negatively skewed, with a clear bias towards highly eccentric pores and a long tail to the left. Mean eccentricity is lower in Gilscocarbon than in PGA. Given the large numbers of highly eccentric pores in each material, it was anticipated that loading-induced changes to mean pore eccentricities would be dominated by deformation of highly eccentric pores. Thus different orientations of PGA graphite are expected to behave very differently due to their highly eccentric, well ordered filler particle pores.

Figure 5.20 shows the variation of mean pore eccentricity in the PGA and Gilscocarbon samples during the application of progressively greater loads.
Each sample was observed to exhibit a linear increase in mean pore eccentricity when the applied load was increased. The compressive strength data in Table 5.2 suggests that Gilsocarbon should exhibit the smallest stress-induced changes in mean pore eccentricity since it has a much higher compressive strength than either orientation of PGA graphite. This hypothesis was confirmed by the data in Figure 5.20, with the rate of change of pore volumes in Gilsocarbon being smaller than the equivalent behaviour in PGA.

Gilsocarbon was observed to predominantly contain highly eccentric pores, but with little preferential directional orientation of pores, as shown in Figure 5.19 and Figure 4.31 respectively. When a compressive load was applied to the Gilsocarbon sample, the pores oriented perpendicular to the loading axis were less resistant to loading-induced collapse and exhibited a relatively large increase in eccentricity. The pores oriented parallel to the loading axis were stiffer and more resistant to deformation, and exhibited a relatively small decrease in eccentricity. When considering all orientations of pores in Gilsocarbon, these competing changes resulted in a net increase in mean eccentricity.
For the PGA-AG sample the rate of change is greater than that for PGA-WG, which was expected since this orientation of PGA has a lower strength and is more susceptible to deformation, as shown in Table 5.2. Long thin pores are more resistant to deformation if they are oriented parallel to the loading axis than if they are oriented perpendicular to the loading axis. In this case the needle-like pores present in the filler particles are oriented perpendicular to the applied axial load, so they are particularly susceptible to deformation. By comparison, the filler particle pores in PGA-WG are much more resistant to compression due to their orientation along the loading axis, which explains the lower rate of change of mean eccentricity observed in the PGA-WG sample.

To explain the observed increases in mean eccentricity in the PGA samples, the effects of the aligned filler particles must be considered. In the PGA-AG sample highly eccentric pores in the filler particles are ordered perpendicular to the loading direction. Pores of this orientation will exhibit an increase in eccentricity when compressed, which contributes to the increase in mean eccentricity.

The filler particles in the PGA-WG sample contain pores ordered parallel to the loading direction. It was expected that compressive loading this would result in a reduction in mean pore eccentricity, however this was not observed. Applying the load to this sample increased the mean eccentricity of the pores as they deformed, but at a lower rate than for the PGA-AG sample.

This behaviour is explained by the pores’ resistance to deformation when compressed along their long axis. The stiffness of these pores will mean that a relatively small reduction in eccentricity occurs when they are compressed. Due to the stiffness of pores in filler particles in this orientation, the contribution of the elongated pores in the filler particles to the overall mean porosity is less in PGA-AG than in PGA-WG. With no preferential orientation of pores present in the non-filler regions, a relatively large mean increase in pore eccentricity in these regions was observed, for the same reasons that underpin the behaviour in Gilsocarbon, discussed above. The large increase in mean pore eccentricity in the non-filler regions and the small decrease in mean pore eccentricity observed in the filler particles combine to give a small net increase in mean pore eccentricity in the PGA-WG sample.

It was anticipated that different shapes, sizes and orientations of pores would behave differently when subjected to compressive loading, hence an investigation was
performed to determine whether any particular pore properties were causing the changes observed in Figure 5.20.

Figure 5.21 below shows the variation of pore eccentricity in Gilsocarbon graphite, but with the pores split into groups based upon their volumes. Five groups were produced, each containing 20% of the total number of pores. Hence the first group contains the largest 20% of the pores, the second group contains the next largest 20%, etc. For each group, mean pore eccentricity was plotted against the ratio of the applied load to the failure load.

![Graph showing variation of pore eccentricity in Gilsocarbon](image)

**Figure 5.21**: Variation of pore eccentricity in Gilsocarbon, with pores split into five groups based upon their volumes. Each group contains twenty percent of the total number of pores.

Three clear trends regarding the relationship between pore volume and pore eccentricity can be seen in Figure 5.21. First, larger pores exhibit greater mean pore eccentricities. As the sizes of the pores in each group decrease, the mean eccentricity value also decreases, but the rate of decrease between different groups is not consistent. The second major observation is that the stress-induced variation of mean pore eccentricity is linear, regardless of the volumes of the pores. This corroborates the linear trend for all pores observed in Figure 5.20. The third important observation is
that the rate of change of mean pore volume is greater for larger pores. The gradients of the best-fitting lines in Figure 5.21 get progressively lower as the volumes of the pores in each group get smaller. This suggests that larger pores are more susceptible to loading-induced deformation, resulting in changes in mean pore eccentricity.

This analysis was repeated for the two PGA samples. Figure 5.22 shows the variation of mean pore eccentricity in the PGA-AG sample, and Figure 5.23 shows the behaviour of the PGA-WG sample. In each case the pores are split into five groups based upon their volumes.

![Graph](image)

Figure 5.22: Variation of pore eccentricity in PGA-AG, with pores split into five groups based upon their volumes. Each group contains twenty percent of the total number of pores.
Similar behaviour was observed in the PGA samples as in the Gilsocarbon sample. In each case the largest pores were the most eccentric, the larger pores exhibited a greater rate of change of mean pore eccentricity than the smaller pores, and the relationships between mean pore eccentricity and applied load were linear for each volume group. The only major difference between the Gilsocarbon and PGA observations is that the values of mean pore eccentricity for each group are relatively evenly spaced in both PGA samples, but not evenly spaced in the Gilsocarbon sample. This suggests that a linear relationship between pore eccentricity and pore volume is present in PGA graphite, but not in Gilsocarbon.

These observations show a clear relationship between the volume of a pore and its propensity for stress-induced deformation, such that applying a compressive load results in an increase in its mean pore eccentricity. However, pore volumes are not the only behaviour expected to influence the rate of variation of eccentricity. As shown in Figure 4.26, variation of pore eccentricity is also strongly dependent on pore orientation in extruded graphite. Further investigation of how pore properties affect
their response to stress growth will yield additional insight into how graphite components deform, and how this deformation can be minimised.

5.6.2.1 Comparison to Confocal Laser Microscopy Data

The tomography data provided information of behaviour of pore eccentricity in three dimensions. The results can be compared to the study of pore eccentricity in two dimensions using confocal laser microscopy data, as discussed in Section 4.8.2, to determine if the two studies of the same property agree with one another.

The range of pore eccentricities observed in each sample at zero load is shown in Figure 5.24. Since the confocal microscopy and tomography samples were different sizes, they contained significantly different numbers of pores. In order to allow comparisons between the two sets of data, the frequency of pores of each eccentricity range is shown as a percentage of the total number of pores.

![Graph showing Range of eccentricities of pores at zero load, calculated using confocal microscopy and tomography.](image)

Figure 5.24: Range of eccentricities of pores at zero load, calculated using confocal microscopy and tomography.

It is clear that for each grade of graphite the behaviour observed using confocal microscopy and using tomography are similar. In each case the same trends are
observed, with a strong bias towards highly eccentric pores, a modal value of 0.85 to 0.95 and a long tail to the left. However, for Gilsocarbon and PGA-WG, the modal eccentricity value is lower in the tomography data than the confocal microscopy data. For PGA-AG, the modal value is greater for the tomography data.

Figure 5.25 shows the stress-induced variation of mean pore eccentricity for graphite samples studied using confocal microscopy and tomography techniques. Since the tomography and microscopy samples were different geometries, different ranges of load were applied, making direct comparisons between Figure 4.25 and Figure 5.20 difficult. To address this issue, the applied compressive loads were measured as a ratio to the anticipated failure load, which enables direct comparisons to be made between both sets of data.

![Graph showing the stress induced variation of mean pore eccentricities in Gilsocarbon and PGA graphite, calculated using confocal laser microscopy and X-ray tomography data.](image)

When comparing the pore area and pore volume data from the confocal microscopy study and the tomography study respectively (as shown in Figure 5.16), a consistent relationship was observed between the two series of data. Unfortunately, no equivalent relationship or trend appears to exist for the pore eccentricity data. For
the Gilsocarbon and PGA-AG samples, the three-dimensional tomography data show a greater response to stress-induced deformation than the confocal microscopy data. However, for the PGA-AG sample, the tomography data exhibits a smaller change in mean pore eccentricity than that observed using the confocal microscopy data. The only consistent behaviour between the two studies is that a loading-induced increase in mean eccentricity is always observed.

The results of this comparison enable an analysis of the suitability of two-dimensional studies of eccentricity, such as that by Kane [56]; and of two-dimensional studies of three-dimensional behaviour in general.

Studies of Poisson’s ratio of graphite have shown Gilsocarbon to have a value of 0.21 [10] and PGA to have values of 0.07 both with and against the grain [17]. This suggests that during the application of an axial load, the majority of sample geometry changes occur along the loading axis, while comparatively little sample expansion is expected to occur along the axes perpendicular to the applied load. These theories were corroborated by a study of the amount of sample expansion occurring in the vertical plane during the confocal microscopy data, as discussed during the two-dimensional nearest-neighbour analyses in Section 4.8.5.1. This suggests that two-dimensional studies of pore eccentricities and three-dimensional studies of pore eccentricities should exhibit similar results, since most of the pore contraction occurs along the axis that the confocal microscope can observe. The addition of a third dimension to the data acquisition process was not expected to significantly change the observed stress-induced deformation behaviour.

The observations in Figure 5.24 suggest that two-dimensional studies of pore eccentricity are reasonable approximations of the actual behaviour which can only be fully observed in three dimensions. Figure 5.25 shows in greater detail the differences in results obtained using the two techniques and, as discussed above, there is no clear trend occurring between the two techniques. This makes it more difficult to quantify the suitability and usefulness of two-dimensional studies of pore eccentricities. However, given that both studies into variation of pore eccentricities produced data with broadly similar behaviours, it appears that two-dimensional studies of pore eccentricity data are valid, and the results are a reasonable qualitative depiction of the physical processes that are occurring.
5.6.3 Pore Surface Areas

The variation of surface areas of pores is another property that can only be studied using three-dimensional data, which is one of the reasons why little research has been conducted into its response to stress. This is unfortunate considering the importance of this parameter on the behaviour of the bulk material. Surfaces of pores that are open to the atmosphere can be considered as open surfaces of the graphite itself. Since the pore structure permeates deep into the graphite components, the greater the surface area of pores present in the sample, the greater the surface area of graphite that is in contact with the active environment in a working reactor, e.g. the gas coolant in an AGR. Many processes that occur in a working reactor, such as oxidation, occur through physical contact. Therefore a greater surface area of open pores should lead to an increase in the rate at which oxidation and other contact processes occur.

After completing the segmentation process discussed in Section 5.4, each individual pore in the samples had been successfully defined. The surface area of each individual pore was calculated with the assistance of the 3D Objects Counter plugin created by Bolte and Cordelières [75] that quantifies multiple different parameters of objects defined through thresholding. The plugin calculated the surface area of each pore by calculating the number of faces of each voxel that act as a boundary for the given pore. The total number of bounding voxel faces for each pore was multiplied by the surface area of each voxel face (derived from the image resolution) to determine the surface area of each pore.

The main errors associated with pore surface area calculations are due to thresholding and voxel size. The error due to thresholding has already been discussed in Section 5.4. The error due to voxel size is difficult to quantify accurately due to the complex shapes of the pores. However, as with the pore volume error calculations, a reasonable approximation of the errors can be calculated by fitting an ellipsoid to each pore and calculating the error in terms of the semi-axis lengths of the ellipsoid. The surface area $S$ of an ellipsoid can be defined in terms of its semi-axes lengths $a$, $b$ and $c$ as follows:

$$S \approx 4\pi \left( \frac{(ab)^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3} \right)^{1/1.6}$$

(5.15)
Considering each pair of axis lengths separately, a new variable $K$ can be defined such that:

$$K = (ab)^{1.6} = a^{1.6}b^{1.6} \quad (5.16)$$

Two further variables $X$ and $Y$ are defined such that:

$$X = a^{1.6}, \quad Y = b^{1.6} \quad \therefore \quad K = XY \quad (5.17)$$

The errors on $X$ and $Y$ are:

$$\sigma_X = 1.6 X \left( \frac{\sigma_a}{a} \right) = 1.6 \sigma_a a^{0.6} \quad (5.18)$$

$$\sigma_Y = 1.6 Y \left( \frac{\sigma_b}{b} \right) = 1.6 \sigma_b b^{0.6} \quad (5.19)$$

Substituting into Equation (5.16), and since the error on voxel size is the same for each axis, a general error term $\sigma$ can be introduced:

$$\left( \frac{\sigma_K}{K} \right)^2 = \left( \frac{\sigma_X}{X} \right)^2 + \left( \frac{\sigma_Y}{Y} \right)^2 = ((1.6\sigma a^{-1})^2) + ((1.6\sigma b^{-1})^2) \quad (5.20)$$

Defining a final new variable $D$ such that:

$$S \approx 4\pi D^{1/1.6}, \quad D = \left( \frac{(ab)^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3} \right) \quad (5.21)$$

The error on $S$ can be defined as:

$$\sigma_S = 4\pi \frac{1}{1.6} D^{1/1.6} \left( \frac{\sigma_D}{D} \right) \quad (5.22)$$
where:

\[
\sigma_d = \frac{1}{3} \left[ \sqrt{(E)^2 + (F)^2 + (G)^2} \right] \quad (5.24)
\]

and:

\[
E = ((ab)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{a} \right)^2 + \left( \frac{1.6\sigma}{b} \right)^2 \right] \quad (5.25)
\]

\[
F = ((bc)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{b} \right)^2 + \left( \frac{1.6\sigma}{c} \right)^2 \right] \quad (5.26)
\]

\[
G = ((ac)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{a} \right)^2 + \left( \frac{1.6\sigma}{c} \right)^2 \right] \quad (5.27)
\]

Figure 5.26 shows rate of change of mean pore surface areas during the application of compressive loads for the two PGA samples and one Gilsocarbon sample.
Figure 5.26: Variation of mean pore surface areas of PGA and Gilsoarbon samples during the application of a range of axial compressive loads. The applied loads are calculated as a ratio to the failure load calculated Equation 4.2.

Before the application of a compressive load, Gilsoarbon was observed to have the smallest mean pore surface area of the three samples. Results for the two PGA samples are much closer to each other, with PGA-WG having a higher mean pore surface area than PGA-AG. At zero load, there should be no difference in the PGA-WG and PGA-AG samples besides standard differences in material composition. Considering the size of the errors associated with pore surface area measurements, it is clear that the difference in mean pore surface areas in the PGA samples is not statistically significant; but the difference between the results for Gilsoarbon and both of the PGA samples is statistically significant.

In each case the mean pore surface area decreased as the applied load increased. This was expected since during the application of the compressive load, the bulk volume of the sample decreased, and it is easier for pores to accommodate this sample shrinkage by collapsing than for the binder or filler phases to shrink. Since mean pore volumes have been observed to decrease, as shown in Figure 5.14, the reduction in pore surface areas was also expected.

The relationship between mean pore surface area and the applied load is best described by a quadratic curve for each sample, as confirmed by linear regression.
analysis. The Gilsocarbon sample exhibited the smallest change in pore surface area per unit volume. This was expected since Table 5.2 shows that Gilsocarbon has the greatest stiffness of the three samples. The data collected on pore volume variation in Figure 5.14 supports this result, since the Gilsocarbon sample also exhibited the smallest change in pore volumes during the application of the load. Pore volumes and pore surface areas are geometrically linked, and this relationship will be discussed further in Section 5.6.3.1.

The PGA samples exhibited a greater amount of pore surface area variation than the Gilsocarbon sample in the range studied. The PGA-WG sample exhibited a smaller change per unit volume than the PGA-AG sample, but the difference between the two is small compared to the difference between the PGA and Gilsocarbon sample behaviours. These results correlate with observations of pore volume variation shown in Figure 5.14, where stress-induced pore volume variation was slightly greater in the PGA-AG sample than the PGA-WG sample.

### 5.6.3.1 Comparison to Pore Volume Data

Pore volume and pore surface area are both parameters of pore size and are geometrically linked, so it is expected that a direct relationship will be observed between them. If the relationship is poor or not observed at all, it would suggest flaws in the characterisation or measurement techniques. In order to determine whether any relationship is present, the ratio between pore volumes and pore surface areas was calculated for each sample, as shown in Figure 5.27.
For both PGA samples the relationship between mean pore volume and mean pore surface area is very well defined by a straight line in the range studied. The quality of the linear fit appeared poorer for Gilsocarbon but, through calculation of residuals, a linear fit was found to be most suitable type of best-fitting line.

For each sample mean pore volume and mean pore surface area exhibited strong positive linear correlation. The gradients of each curve, representing change in pore volume observed per unit change in pore surface area, vary between samples. Therefore it does not appear possible to define a single quantitative relationship that applies for all samples; unlike the relationship that was defined for pore areas and volumes using Figure 5.16.

The results in Figure 5.27 were compared to the surface area-volume relationships for a sphere and a number of Platonic solids. Figure 5.28 shows the results from Figure 5.27 alongside data showing the relationship between volume and surface area for a sphere, a cube and a tetrahedron. Figure 5.29 shows a subsection of Figure 5.28 that focuses on the region containing the experimental data.
Figure 5.28: Relationship between mean pore volume and mean pore surface area for Gilsocarbon and PGA samples, with lines showing the volume-surface area relationship for a sphere, a cube and a tetrahedron.

Figure 5.29: A subsection of Figure 5.28 focussing on the region containing the experimental data on pore sizes.
The data for the sphere, cube and tetrahedron show that the surface area to volume ratio decreases with increasing volume. However, there is not enough evidence to determine whether this is the case for the pores in graphite, since the data occupies too narrow a range of sizes.

The data for each graphite sample appear to follow a similar trend to the tetrahedron in the range studied. It appears that for a given volume, the surface area is greater for rounder shapes, and as the shape becomes less round and more angular, the rate of change of volume per unit surface area increases. During the pore eccentricity study, a high prevalence of highly eccentric pores was observed, as shown in Figure 5.19. Since a high eccentricity represents deviation from roundness, the eccentricity data agrees with the observation of the relatively high measurements of pore volume to surface area ratios.

The observation that pores in graphite exhibit similar volume and surface area properties to tetrahedrons was unexpected. It was considered that this behaviour could be caused by the techniques used to study the samples. The confocal laser microscopy and X-ray tomography images are comprised of pixels and voxels respectively, which may give the pores an artificially angular morphology. However, if this were occurring, it was expected that the pore data in Figure 5.29 would be best described by the cubic area-volume relationship, as opposed to the tetrahedron relationship. Also, the application of lower thresholds for pore size, as discussed in Section 4.8.1, should ensure that the pores being studied were made up of a suitable number of pixels and voxels to be reasonable representations of the actual pores.

The surface area to volume ratio is a measure of compactness [80]. It is a parameter that has important applications in a number of fields. It has already been discussed that processes such as oxidation occur faster when a larger surface area is available, among other factors. There are also processes that are affected by both surface area and volume. The greater the surface area to volume ratio of a material, the faster the material will respond to changes in the conditions of the environment. This can affect mechanisms such as heat transfer and propagation of thermal stresses through graphite components. Hence surface area to pore volume ratios can be combined with relevant heat transfer data to provide insight into growth of thermal stresses, for example.
5.6.4 Pore Angularity

In Section 4.8.4, a novel technique was created to study the variation of a measure of pore angularity in two dimensions. This new method was adapted from an existing technique [67], and involved comparing the perimeter of each pore with the perimeter of an ellipse fitted to each pore using Fiji image analysis software. The difference between the actual perimeter of the pore and the perimeter of the fitted ellipse, with the ellipse having zero angularity, can be used to quantify the degree of angularity of the pore.

This novel technique was extended to three dimensions to estimate a measure of angularity for pores using the tomography data. Since the entire surface of each pore can now be studied, it was decided that the surface area of a pore and the surface area of its fitted ellipse could be used to extend the technique into three dimensions. The greater the difference between the surface area of the pore and the surface area of the ellipse, the more rough and irregular the surface is. Once all pores in the sample have been considered, the average value is defined as the mean measure of angularity.

The main sources of error associated with calculations of pore surface areas are the error due to thresholding and the error due to pixel size. The error due to pixel size was calculated in Section 5.6.3, in Equations (5.23) to (5.27):

\[
\sigma_s = \frac{4\pi}{1.6} \left( \frac{(ab)^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3} \right)^{1/16} \left( \frac{\sigma_D}{\frac{(ab)^{1.6} + (ac)^{1.6} + (bc)^{1.6}}{3}} \right) \quad (5.23)
\]

where:

\[
\sigma_D = \frac{1}{3} \left[ \sqrt{(E)^2 + (F)^2 + (G)^2} \right] \quad (5.24)
\]

and:

\[
E = ((ab)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{a} \right)^2 + \left( \frac{1.6\sigma}{b} \right)^2 \right] \quad (5.25)
\]

\[
F = ((bc)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{b} \right)^2 + \left( \frac{1.6\sigma}{c} \right)^2 \right] \quad (5.26)
\]
\[ G = ((ac)^{1.6})^2 \left[ \left( \frac{1.6\sigma}{a} \right)^2 + \left( \frac{1.6\sigma}{c} \right)^2 \right] \] (5.27)

The error associated with pixel size was combined with the error due to thresholding to calculate the total error associated with pore surface area values.

Values of mean measure of angularity were calculated for each sample at a range of applied loads, and the results are shown in Figure 5.30.

![Figure 5.30: Rate of change of the measure of angularity with increasing stress for Gilsocarbon and PGA samples.](image)

The mean measure of angularity for Gilsocarbon exhibited very little change during the application of a compressive load. Studying the data by eye suggested that the measure of angularity remained unchanged but, by applying a linear fit to the data, a small downward trend with increasing applied load is observed.

Pore volume data in Figure 5.14 shows that the pores in Gilsocarbon are contracting, but the data in Figure 5.30 suggests that the contraction is occurring in such a manner that the microstructures of pores are not becoming significantly smoother or rougher. The two PGA samples exhibit much clearer trends when compressed. Both the PGA-AG and PGA-WG samples show an increase in the mean
measure of angularity when subjected to a compressive load. This suggests that compressive loading makes the measured surface of the pores more rough and uneven.

The rate of change of angularity per unit load is greater for the PGA-AG sample than for the PGA-WG sample, by a factor of approximately 2.2. Since PGA-WG has a higher stiffness than PGA-AG, it was expected that the PGA-WG sample would be more resistant to loading-induced dimensional change.

These results suggest that the orientation of pores in a PGA sample will affect the rate of change of angularity per unit applied load, but has no effect on whether the surface of the sample becomes more or less rough. Therefore, another variable must affect whether a positive or negative change in the mean pore angularity is observed.

5.6.4.1 Comparison to Confocal Laser Microscopy Data

The results discussed in Section 5.6.4 provide insight into the behaviour of angularity of pores in three dimensions. These results can be compared to the two dimensional study of pore angularity, discussed in Section 4.8.4, to determine if the two studies of the same property agree with one another.

It is difficult to compare the results in Figure 4.35 and Figure 5.30, showing mean measures of angularity using confocal microscopy data and tomography data respectively, for a number of reasons. The sample sizes and geometries for each technique were different, so the loads that the samples could withstand varied greatly. Therefore, it was decided that the data should be plotted as ratios to the expected failure load of each sample.

Also, the values of mean measure of angularity observed using each technique were significantly lower for the tomography data than the confocal microscopy data. This is due to the differences in attainable resolutions for each technique. The confocal microscopy data had a much greater resolution than the tomography data. Therefore, much more detail could be observed and smaller regions of surface roughness could be considered when calculating the measure of angularity for each pore. In order to compare the two sets of data, the results for each sample were normalised with respect to the measurement at zero load, i.e. the zero-load value was set to one and higher loads were defined by a ratio to this figure.
After applying the above techniques to the data, the confocal microscopy and tomography data were plotted together in Figure 5.31.

![Figure 5.31: Mean measures of angularity for PGA and Gilsocarbon samples, calculated using confocal microscopy and X-ray tomography. The applied load is shown as a ratio to the failure load, and measures of angularity are normalised to the zero load result.](image)

The differences between data acquired using confocal microscopy and using X-ray tomography are clear in Figure 5.31. For each material the results obtained from tomography show a much greater change in mean measure of angularity than the results obtained using confocal microscopy. Ratios of the gradients of each best-fitting line were calculated for each pair of samples to determine whether the relationship between results for confocal microscopy and for tomography were consistent. Since the tomography data for PGA-AG is best defined by a quadratic curve, the mean value of the gradient was used for the ratio calculations. The results are shown in Table 5.5.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate of change – X-ray tomography</th>
<th>Rate of change – confocal microscopy</th>
<th>Modulus of ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gilsocarbon</td>
<td>-0.0594</td>
<td>-0.0010</td>
<td>59.4</td>
</tr>
<tr>
<td>PGA-AG</td>
<td>0.2184</td>
<td>0.0173</td>
<td>12.6</td>
</tr>
<tr>
<td>PGA-WG</td>
<td>0.1298</td>
<td>-0.0081</td>
<td>16.0</td>
</tr>
</tbody>
</table>

Table 5.5: The rate of change of the mean measure of angularity due to growth of stresses, and the ratio between these variables.

The ratio values shown in Table 5.5 show the difference between the rates of change of angularity for each technique. The ratios for the two PGA samples, 12.6 and 16, are similar in magnitude, but PGA-AG increased and PGA-WG decreased as the applied load increased. The ratio for Gilsocarbon, however, was significantly greater. This may be due to the fact that the confocal microscopy data showed very little loading-induced change and the gradient was very close to zero.

Clear numerical relationships between the confocal microscopy data and tomography data were observed for pore size parameters in Sections 5.6.1.1 and 5.6.3.1. In this case it is not clear whether such a relationship has been observed. Further studies may confirm whether the similarities in gradient ratios for the PGA samples are statistically significant and indicative of a greater trend. However, it appears that any trend present breaks down for Gilsocarbon, which experiences too little loading-induced change in the mean measure of angularity to define a clear trend.

Aside from the gradients of the best-fitting lines, the Gilsocarbon and PGA-AG data exhibit similar behaviour for both techniques. Gilsocarbon samples experienced the smallest amount of loading-induced variation of angularity for both the tomography and confocal microscopy techniques, and the PGA-AG samples exhibited the greatest change per unit applied load. However, the PGA-AG sample analysed using tomography exhibited behaviour best described by a quadratic curve, while all the other samples exhibited a linear relationship, as confirmed through regression analysis. The PGA-WG tomography sample could be described by both a straight line and a quadratic curve, but regression analysis suggests that while both are well fitting, the linear fit is marginally more suitable in this case. The Gilsocarbon tomography data is well described by a linear fit.
The most significant difference between the two sets of data is the behaviour of the PGA-WG samples. When analysed using confocal microscopy, the mean measure of angularity was found to decrease linearly. When the same material was analysed in three dimensions using X-ray tomography, a linear increase of the mean measure of angularity was observed during the application of compressive loads. It is not clear why this conflict exists, given the general agreement between confocal microscopy and tomography measurements for other pore structural parameters are discussed in Sections 5.6.1.1, 5.6.2.1 and 5.6.3.1.

5.7 Conclusions

Many previous imaging studies into pore behaviour in graphite, such as those by Kane et al. [56], Bodel [46] and Taylor et al. [81], as well as those discussed in Chapter 4, utilise two dimensional microscopy data. The extension of these existing methodologies to three dimensions allows analysis of the pore structure in the interior of the materials to be performed. This yields information that is much more useful and relevant to the study of graphite moderator materials than could be achieved solely through the acquisition and analysis of two dimensional data.

At low loads, application of compressive loads was found to predominantly deform the pores and cracks, with a proportionally smaller amount of binder phase closure. The relationship between pore volumes and applied load was found to be inversely quadratic. This is in contrast to research by the authors using two dimensional data, which predicted an inverse linear relationship between pore area and applied load. Since the existence of porosity in the graphite moderating components is known to weaken the components’ strength, stress-induced closure of pores is expected to make graphite reactor components stronger and have increased longevity in a working reactor. However, this effect does not happen in isolation – for example, the competing processes of oxidation and irradiation-induced damage will hasten the damage and degradation to the material, reducing its strength and structural integrity.

Greater agreement between two-dimensional and three-dimensional techniques was observed when studying the variation of pore eccentricity. Using the X-ray tomography technique, applying a compressive load to the samples resulted in a linear increase in mean pore eccentricity, and the largest pores in the samples
exhibited the greatest amount of eccentricity variation per unit of applied load. Comparing these results to the confocal laser microscopy data showed that both techniques observed a linear increase in mean pore eccentricity during stress generation, but no consistent numerical relationship could be identified between the rates of change for the two techniques.

Pore surface areas were found to decrease quadratically with increasing load, and a linear relationship between mean pore volume and mean pore surface area was observed. When this relationship was compared to the volume-surface area relationship for a number of Platonic solids, the morphology of the pores in both Gilsocarbon and PGA were found to be best described by a tetrahedron. This observation may prove useful when attempting to model behaviour of graphite components using appropriate computer software, since it suggests that the pores in graphite are best described by tetrahedrons, as opposed to the spheres or ellipsoids that a visual analysis of microscopy images would suggest.

Lastly, the stress-induced changes to mean pore angularity were found to vary depending on the orientation of the PGA samples with respect to the grain direction, while the Gilsocarbon sample exhibited a small decrease in the mean measure of angularity. No consistent relationship between the confocal laser microscopy data and the X-ray tomography data could be defined.

There are two main limitations on the data and conclusions presented in this chapter. The first limitation is the limited resolution of the data available. This is due to the size of the axial deformation rig increasing the source-to-sample and sample-to-detector distances. While the Nikon Metrology 320/225 kV Custom Bay can achieve resolutions of 3 µm, the size of the rig resulted in a maximum attainable resolution of 18.5 µm. Repeating the experiments documented in this chapter with a smaller rig will result in a significant increase in the number and range of sizes of resolvable pores, particularly given the significant bias towards small pores shown in Figure 5.11 and Figure 5.12.

The second limitation is due to the small number of samples studied. Due to a number of constraints including limited time and funding, only a single series of X-ray tomography scans could be performed for each grade and orientation of graphite. However, as discussed in the context of the confocal laser microscopy experiments in Section 4.10, the author believes that the observations presented in this chapter are
both reliable and statistically significant. Each sample studied contained in excess of one hundred thousand pores, and the samples themselves were large enough to be considered representative of the bulk material. Although studying more samples from the same graphite block is not expected to yield significantly different results to those presented above, using more samples would further corroborate the conclusions made in this chapter.

Overall, the three-dimensional analyses performed in this chapter have yielded significant insight into the response of graphite to the build-up of stresses. Since microstructural deformation is a three-dimensional mechanism, the advantages of using X-ray tomography over optical microscopy and confocal laser microscopy for data collection are clear. However, the fact that a number of parameters exhibited similar variation using both X-ray tomography data and confocal microscopy data suggests that while there is an undeniable advantage of analysing three-dimensional processes using three-dimensional techniques, there are cases where sub-three-dimensional techniques provide data that is just as useful. Since there is more existing literature that uses two-dimensional techniques than three-dimensional techniques for graphite microstructural analysis, and since the former is typically quicker, easier and requires less specialised equipment, the confirmation of the continued usefulness and relevance of two-dimensional imaging techniques is reassuring.

5.8 Summary

- A series of in-situ tomography experiments were performed during the application of axial compressive loads to determine how the pore structure varies during the build-up of stresses. Images were analysed in Fiji and Avizo to acquire quantitative data regarding various properties of open pores.
- The novel technique created in Section 4.7 to quantify the errors associated with the imprecise segmentation process was adapted and extended for use with three dimensional data.
- The stress-induced variation of pore volumes was studied in three dimensions. At zero load, frequency of pores of a given volume decreased with increasing size by a power law for each sample. During load application, mean pore
volumes were observed to decrease quadratically for all samples, with pore orientation having a significant effect on the rate of volume change.

- Pore volume data were compared to pore area data acquired using confocal microscopy. Mean pore areas were found to be four times more responsive to loading-induced contraction than mean pore volumes. These results enabled an analysis of the usefulness of two-dimensional studies for three-dimensional phenomena.

- Variation of mean pore eccentricity was studied at a range of applied loads. The novel technique for eliminating poorly-fitting ellipses defined in Section 4.8.2 was extended to three dimensions. Each sample was dominated by high eccentricity pores, and data were negatively skewed. A linear increase in mean pore eccentricity with increasing load was observed. Larger pores were found to be more eccentric and exhibited greater loading-induced changes to eccentricity than smaller pores.

- Two-dimensional and three-dimensional analyses of pore eccentricity variation were compared. Although no consistent numerical relationship between the two sets of data could be defined, a study of the effects of Poisson’s ratio on the data suggest that both two- and three-dimensional studies represent reasonable analyses of pore eccentricity variation.

- Access to three-dimensional data enabled the analysis of how pore surface areas were affected by stresses. Mean pore surface areas were found to decrease quadratically during the application of an axial load.

- Strong linear correlation was observed between the pore surface area data and pore volume data. Comparing the surface area-volume relationship with a number of Platonic solids, the pores were observed to behave similarly to tetrahedrons.

- The novel technique for quantifying a measure of angularity was extended to three dimensions. Gilsocarbon exhibited a small decrease in mean measure of angularity, while both PGA samples exhibited an increase.

- The tomography and confocal microscopy data for mean measures of angularity were compared. The PGA-WG samples unexpectedly showed conflicting behaviour, with an increase observed using tomography and a
decrease observed using confocal microscopy. The differences in the PGA data were proportionally similar for each sample.
Chapter 6: X-Ray Crystallography Experiments

This chapter discusses a series of experiments performed using the third of three main experimental techniques selected for use for this project, X-ray crystallography.

Chapters 4 and 5 utilise imaging techniques to study the stress-induced deformation behaviour of graphite samples. The main limitation of imaging studies is that the usefulness of the data collected is governed by the resolution of the imaging apparatus. Any phenomena that occur at length scales below the resolution of the images are not observable. The confocal microscopy and tomography data had resolutions of the order of microns, so any behaviour occurring below this threshold was not studied.

As discussed in Section 2.1, the growth of stresses in graphite moderator components is known to cause damage to the atomic structure of the graphite. This damage may change the behaviour of the material itself. Since the graphite components used in nuclear reactors are designed and manufactured precisely for neutron moderation, severe deformation to the crystal structure of graphite will change its ability to function as an efficient moderator.

Therefore, it was decided that a study should be performed into how stress growth affects the atomic structure of graphite. The behaviour of the atomic lattice is governed by processes at the Angstrom scale, so traditional imaging techniques were deemed to be of little use for this experiment. Instead, a technique known as X-ray crystallography was used to study the atomic structure of graphite.

6.1 Introduction to X-Ray Crystallography

X-ray crystallography is a technique used for analysis of the atomic and molecular structure of a crystal. A crystal is defined as a material whose atoms or molecules are arranged in an ordered, repeating structure. The repeating structure is known as a crystal lattice. Figure 1.4 and Figure 1.5 show that graphite is comprised of a hexagonal lattice structure, with highly ordered layers of carbon atoms held together in a repeating structure. Therefore, graphite is considered a crystal and can be analysed by X-ray crystallography.
X-rays are useful for the analysis of atomic structures because they exhibit wavelengths between 0.1 Å and 100 Å, which is often similar to the distances between atoms in the repeating lattice structure. This means that X-rays can diffract around single atoms. This property is used in one of the most popular and effective types of X-ray crystallography, known as X-ray diffraction.

6.1.1 Theory of X-ray Diffraction

The technique of X-ray diffraction involves projecting a beam of X-rays onto a crystal. The X-rays will diffract around the lattice planes, and multiple X-rays incident upon the crystal will scatter and interfere with one another. When the beams reach a detector, the interference behaviour at the surface of the detector will produce a diffraction pattern, which can be used to quantify important parameters of the crystal structure.

Figure 6.1 shows a schematic of a simple X-ray diffraction setup. X-rays from an X-ray source travel through a collimator to focus the beam before hitting the crystalline material. A filter may also be placed between the X-ray source and the sample to reduce unwanted parts of the X-rays’ energy spectra. After hitting the sample, the scattered waves interfere with each other and the resulting diffraction pattern is recorded by the detector.

Figure 6.1: Schematic of an X-ray diffraction apparatus.
After a single scan has been performed, the sample is rotated slightly. This varies the angle at which the X-rays hit the sample. The sample is rotated through a range of angle $\vartheta$ values, typically 0° to 90°; while the detector is rotated through $2\vartheta$, since for every degree the sample is rotated, the diffracted beam’s propagation direction will change by two degrees.

The output is a continuous diffraction pattern, with peaks representing angles at which strong constructive interference occurs. Each peak is associated with a set of Miller Indices, which define the lattice planes in the material.

The diffraction pattern can be used to quantify important parameters that define the structure of the crystal lattice, perform phase identification and detect any impurities present in the sample. By comparing the observed peak positions, heights and widths with data from the PDF-4 database, an indexed repository of reference data maintained by the International Centre for Diffraction Data (ICDD), it is possible to confirm the material composition of each sample.

6.2 Materials and Apparatus

6.2.1 The X-Ray Diffraction Scanner

The X-ray diffraction experiments were performed using the Philips Automatic Diffractometer at the University of Manchester. This machine was selected due to its ability to acquire precise X-ray diffraction data, its suitability for use with graphite samples and its rapid data acquisition speeds. Table 6.1 shows the main operational properties of the diffractometer.

The Philips Automatic Diffractometer is ideal for studying the diffraction pattern of graphite. However, a limitation of this apparatus is that it is not possible to perform measurements of the diffraction pattern while using in-situ sample environments, such as compression rigs. There were no diffractometers at the University of Manchester that were compatible with any available compression rigs, which meant that the X-ray diffraction studies could only be performed using prestressed samples. Given that Chapters 4 and 5 involved the collection of extensive amounts of in-situ data, it was unfortunate that this could not be continued for the X-
ray diffraction studies. The consequences of this issue are discussed in more detail in Section 6.5.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration</td>
<td>2θ Bragg Brentano</td>
</tr>
<tr>
<td>Source</td>
<td>Copper anode</td>
</tr>
<tr>
<td>Power</td>
<td>50 kV, 40 mA</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Graphite</td>
</tr>
<tr>
<td>Angle range</td>
<td>5-146°</td>
</tr>
<tr>
<td>Maximum sample size</td>
<td>25 x 25 x 25 mm</td>
</tr>
</tbody>
</table>

Table 6.1: Operational parameters of the Philips Automatic Diffractometer used in the XRD experiments.

6.2.2 The Axial Compression Rig

As discussed in Section 6.2.1, it was not possible to perform in-situ X-ray diffraction experiments since no X-ray diffractometers were compatible with any of the in-situ compression rigs. Instead, it was decided that the samples would be stressed prior to the experiments. As shown in Section 4.3, graphite samples may not fully recover after a compressive load is applied and then fully removed. Thus by prestressing the samples prior to performing X-ray diffraction analysis, the effects of stress-induced deformation can be studied, although the results will be limited to non-recoverable stresses only.

The compression rig manufactured by Deben, previously used during the confocal microscopy experiments, was used to pre-stress the samples prior to undergoing X-ray diffraction. The rig consisted of a static base plate upon which the sample was mounted, with a moveable upper plate and a 5 kN load cell used to apply the compressive load. Integrated software allowed real-time control and tracking of the force applied to the sample, to an accuracy of 0.1 N.

6.2.3 Samples and Sample Preparation

As discussed in Section 3.2.3, a series of cylindrical samples were machined by the machining shop in the University of Manchester’s School of Mechanical, Aerospace
and Civil Engineering. These samples were machined into cylinders of approximate diameter 7 mm and height 2-4 mm. The samples underwent a brief polishing process to produce a reasonably smooth surface. Impurities were removed by placing the sample in an ultrasonic bath containing acetone for twenty minutes.

The properties of the samples used for the X-ray diffraction experiments are shown in Table 6.2.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material</th>
<th>Volume [mm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G008</td>
<td>Gilsocarbon</td>
<td>192.87</td>
</tr>
<tr>
<td>G009</td>
<td>Gilsocarbon</td>
<td>197.29</td>
</tr>
<tr>
<td>G010</td>
<td>Gilsocarbon</td>
<td>201.28</td>
</tr>
<tr>
<td>G011</td>
<td>Gilsocarbon</td>
<td>189.98</td>
</tr>
<tr>
<td>G012</td>
<td>Gilsocarbon</td>
<td>187.65</td>
</tr>
<tr>
<td>G013</td>
<td>Gilsocarbon</td>
<td>201.87</td>
</tr>
<tr>
<td>P007</td>
<td>PGA-WG</td>
<td>192.42</td>
</tr>
<tr>
<td>P008</td>
<td>PGA-WG</td>
<td>192.78</td>
</tr>
<tr>
<td>P009</td>
<td>PGA-WG</td>
<td>187.45</td>
</tr>
<tr>
<td>P010</td>
<td>PGA-WG</td>
<td>199.01</td>
</tr>
<tr>
<td>P011</td>
<td>PGA-WG</td>
<td>192.61</td>
</tr>
<tr>
<td>P012</td>
<td>PGA-WG</td>
<td>187.73</td>
</tr>
<tr>
<td>P107</td>
<td>PGA-AG</td>
<td>191.28</td>
</tr>
<tr>
<td>P108</td>
<td>PGA-AG</td>
<td>187.60</td>
</tr>
<tr>
<td>P109</td>
<td>PGA-AG</td>
<td>192.33</td>
</tr>
<tr>
<td>P110</td>
<td>PGA-AG</td>
<td>193.31</td>
</tr>
<tr>
<td>P111</td>
<td>PGA-AG</td>
<td>192.43</td>
</tr>
<tr>
<td>P112</td>
<td>PGA-AG</td>
<td>194.01</td>
</tr>
</tbody>
</table>

Table 6.2: Details of the samples upon which X-ray diffraction analysis was performed.
6.3 X-Ray Diffraction

The Philips Automatic Diffractometer at the University of Manchester was used to perform the X-ray diffraction. The settings used to produce the initial diffraction pattern are shown in Table 6.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting angle</td>
<td>10°</td>
</tr>
<tr>
<td>Finishing angle</td>
<td>80°</td>
</tr>
<tr>
<td>Step size</td>
<td>0.05°</td>
</tr>
<tr>
<td>Time per step</td>
<td>2s</td>
</tr>
</tbody>
</table>

Table 6.3: The scanning parameters used for the XRD analysis of PGA and Gilsocarbon samples.

The experimental procedure was identical for each sample. The sample was mounted onto a sample holder using ‘Black Tack’ adhesive putty, with care taken to ensure that the flat surface of each sample was parallel to the surface of the sample holder, and hence perpendicular to the X-ray source in the 0° position. Failure to mount the sample in this manner would result in the angle between the sample and the X-ray source being improperly calculated, and the resulting diffraction pattern would be shifted.

A 21 position automatic sample changer was available for use with the diffractometer. The sample holders were mounted onto the sample changer, such that each sample would be automatically scanned in order, with no user intervention required between scans.

The X-rays were emitted at a range of angles between 10° and 80°, since all of the important diffraction peaks for Gilsocarbon and PGA occur within this range. A step size of 0.05° was selected to produce a smooth diffraction pattern and to enable high precision calculations to be made from diffraction pattern parameters, such as measurement of peak widths. The time for each scan was set to 2 seconds, which represented a suitable compromise between data quality and rapid scan times. Hence an overall scan time of approximately 80 minutes was required for each sample.
During each scan, collimated X-rays were emitted onto the sample at angles between 10° and 80° measured clockwise from the plane at which the sample stage resides. The diffracted X-rays were recorded by the detector, which was rotated through an angle of 140°.

The intensity of the X-rays reaching the detector was plotted as a function of the angle of the X-ray detector. Known as a ‘diffraction pattern’, this type of graph yields valuable information regarding the crystallographic parameters that underpin the structure of the crystal lattice and ultimately defines the material’s behaviour. The application of pre-stresses as discussed in Section 6.2.2 damaged the microstructure of the samples, and it is proposed that damage to the crystal lattice has also occurred. Hence by studying changes to the diffraction pattern, it was proposed that the damage could be quantified, as discussed in Section 6.4.

6.4 Diffraction Spectra Analysis

The following figures show examples of the diffraction spectra that were produced using X-ray crystallography. Figure 6.2 shows the diffraction pattern for the GilsoCarbon sample, Figure 6.3 shows the diffraction pattern for the PGA-AG sample and Figure 6.4 shows the diffraction pattern for the PGA-WG sample. The Miller Indices of each peak is shown on the diffraction patterns. Each of the figures shows data before any stresses had been generated in the samples. The x-axis shows the 2θ value, which represents the position of the detector, and the y-axis shows the intensity of the X-rays reaching the detector.
Figure 6.2: Diffraction pattern for the Gilsoarbon sample.

Figure 6.3: Diffraction pattern for the PGA-AG sample.
X-ray diffraction analysis of graphite samples is a well-established technique for the study of the material’s crystal structure, and there is a large amount of existing research available into the crystal structure of unstressed graphite. Therefore only a brief discussion of the unstressed sample behaviour is provided, since these analyses are available elsewhere, and the stress-induced deformation behaviour is of more interest.

As shown in Figure 6.2 - Figure 6.4, each diffraction pattern shows a sequence of data points that indicate the amount of X-rays that are diffracting off the graphite samples and reaching the detector. The x-axis shows the 2θ position, measured in degrees, while the y-axis shows the amount of radiation reaching the detector in units of ‘counts’. In a single diffraction pattern the absolute value of a peak height is not important. The relative heights of different peaks are more important, which is why the somewhat arbitrary unit of ‘counts’ can be used on the y-axis.

The X-ray diffraction patterns of each of the three graphite samples exhibit similar properties. Five clear peaks are observed. The 002 peak occurs at approximately 26° and is by far the largest and narrowest of the peaks in each sample. The 100 and 101 peaks occur at approximately 42° and 44° and are not discrete, since the two peaks
share the same tail region between the peaks. This makes the subsequent calculation of peak widths more difficult. In each case the peak at 44° is wider and taller. The 004 peak occurs at 54°, while the 110 peak is observed at 77°.

The presence of lattice preferred orientation of grains within graphite samples can have significant effects on the intensity distribution of the observed diffraction pattern. Preferred orientation has been observed to affect the intensity of the peaks, such that clear differences may be observed when comparing the diffraction patterns of a solid graphite sample and a powder sample. This will also affect the values of crystal lattice parameters that are calculated from the intensities and widths of the peaks.

To compare the relative heights of the peaks for each sample, the data were normalised. Figure 6.5, Figure 6.6 and Figure 6.7 show the Gilsocarbon, PGA-AG and PGA-WG data respectively, but with the y-axis normalised such that each data point represents the percentage of all counts observed across the full diffraction pattern.

Figure 6.5: Diffraction pattern for the Gilsocarbon sample, with the y-axis normalised.
Figure 6.6: Diffraction pattern for the PGA-AG sample, with the y-axis normalised.

Figure 6.7: Diffraction pattern for the PGA-WG sample, with the y-axis normalised.

The most obvious difference between the peak heights of the three samples is the behaviour of the first peak. This peak is largest for the PGA-AG sample and smallest for the PGA-WG sample, with the Gilscocarbon sample in between. The fourth peak in each sample follows the same trend. However, this behaviour is reversed for the
second, third and fifth peaks – PGA-WG exhibits the tallest peaks, followed by Gilsocarbon, and the peak heights in PGA-AG are the smallest.

As well as identifying the angles at which strong peaks occur, the diffraction spectra shown above can be used to quantify a range of important crystallographic parameters that may be affected by the growth of stresses. By studying the variation of the diffraction spectra in samples that have been exposed to a compressive prestress, the variation of these parameters can be quantified, hence the effects of stress on the crystal structure of graphite can be inferred.

The properties selected for study were:

- The Miller Indices that are used to define the crystal structure.
- The spacing between consecutive lattice planes, known as the ‘crystal layer spacing’ or ‘d-spacing’.
- The unit cell dimensional parameters, known as ‘a-spacing’ and ‘c-spacing’.
- The crystallite size of the material.
- The quantification of internal strains calculated using the Williamson-Hall method.
- A measure of the degree of anisotropy present in the material, known as the Bacon Anisotropy Factor.

Each of the above parameters were studied at a range of applied loads in Gilsocarbon, PGA-AG and PGA-WG samples. Data were collected from multiple samples of each grade of graphite at each level of applied load. Sections 6.4.1 to 6.4.5 discuss the physical significance of each parameter, the calculation method, the observed results for the Gilsocarbon and PGA samples, and the relevance of each parameter to the stress-induced deformation behaviour of the samples.

### 6.4.1 Miller Indices

Miller indices are used to define the orientation of a set of planes within the crystal lattice, with respect to the unit cell. Typically three indices are used – $h$, $k$ and $l$ – which denote the planes orthogonal to Equation (1.1):

$$h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$  \hspace{1cm} (6.1)
where \( \mathbf{b}_{1,2,3} \) are the basis vectors of the reciprocal lattice. The Miller indices are defined in the form ‘(h,k,l)’. Figure 6.8 shows some simple examples of Miller indices for a cubic unit cell.

![Miller Indices for a cubic unit cell](image)

**Figure 6.8**: Miller Indices of certain planes in a cubic cell. Image courtesy of Felix King [82].

Defining Miller Indices for a graphite unit cell is more complicated due to the hexagonal structure of graphite. Three directions \( a, b \) and \( c \) are defined as shown in Figure 6.9.

![Miller indices for a hexagonal crystal](image)

**Figure 6.9**: Miller indices for a hexagonal crystal. The three highlighted planes are crystallographically equivalent to one other.
The three planes highlighted are crystallographically similar, but this is not clear from the Miller Indices. To overcome this problem, a fourth index is defined. The index \( i \) is defined using the \( d \) axis as shown in Figure 6.10, such that:

\[
i = -(h + k)
\]

(6.2)

Now the indices for the three planes look similar to one another. This is known as Miller-Bravais notation. The Miller-Bravais indices are defined in the form \( 'h,k,i,l' \).

To perform phase identification and define the Miller Indices for a sample, the diffraction spectra were compared to a database of specimens known as ‘PDF-4’ (Powder Diffraction File 4) maintained by the International Centre for Diffraction Data. PDF-4 contains diffraction spectra for a large number of different materials. By comparing the diffraction spectra shown in Figure 6.2, Figure 6.3 and Figure 6.4 with the spectra in the database, the material composition of the graphite samples can be confirmed, the presence of any impurities in the samples will be highlighted, and the Miller Indices of the crystal lattice can be defined.

Figure 6.11 shows the diffraction pattern for graphite within the PDF-4 database. By comparing this pattern with the data collected from the X-ray diffractometer, it is clear that the experimental data and reference data are an
excellent match. This confirms that the material is indeed graphite. The lack of any peaks present in the experimental data but not the reference data suggests that there are no significant impurities in the samples. This was expected since the graphite samples underwent a stringent manufacturing process designed to remove impurities, as discussed in Section 1.4.

![Diffraction pattern for graphite](image)

Figure 6.11: Diffraction pattern for graphite taken from the PDF-4 database maintained by the International Centre for Diffraction Data (ICDD).

By comparing the reference data to the experimental data, it was also possible to define the Miller Indices for each peak. Table 6.4 shows the Miller and Miller-Bravais Indices for the five peaks in each of the samples.

<table>
<thead>
<tr>
<th>Peak Angle[^°]</th>
<th>Miller Indices</th>
<th>Miller-Bravais Indices</th>
<th>d-spacing [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>002</td>
<td>0002</td>
<td>3.42</td>
</tr>
<tr>
<td>42</td>
<td>100</td>
<td>1010</td>
<td>2.14</td>
</tr>
<tr>
<td>44</td>
<td>101</td>
<td>1011</td>
<td>2.06</td>
</tr>
<tr>
<td>54</td>
<td>004</td>
<td>0004</td>
<td>1.70</td>
</tr>
<tr>
<td>77</td>
<td>110</td>
<td>1120</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 6.4: Miller and Miller-Bravais indices and d-spacings for the peaks in the Gilsocarbon and PGA samples.
6.4.2 Unit Cell and Layer Spacing Parameters

Three important parameters of the graphite crystal lattice can be calculated using Bragg’s law for scattering from a crystal lattice [83]. Bragg’s law relates the spacing between consecutive layers in a crystal to the scattering angles at which X-rays of a known wavelength are observed to interfere constructively. Figure 6.12 shows how Bragg’s law can be derived for a crystal.

Figure 6.12: The derivation of Bragg’s Law between two layers of a crystal lattice. For constructive interference of two X-rays to occur, the path length difference, \(2d \sin \theta\), must be an integer number of wavelengths.

The top two layers of carbon atoms in the crystal lattice are shown. X-rays are directed upon the surface of the material and, depending on whether or not they collide with a carbon atom, they will either continue deeper into the sample or scatter off an atom. It is statistically unlikely that an X-ray will penetrate through the entire sample without scattering off an atom.

The scattered X-rays will propagate in a different direction and interfere with other scattered X-rays. X-rays that are in phase with one another, meaning that the difference in distances travelled between the two rays is an integer number of wavelengths, will interfere constructively. This results in a new wave with peak amplitude greater than that of the individual waves. X-rays that are out of phase with one another, meaning that the path length distance is a non-integer number of wavelengths, will interfere destructively. This can result in a new wave with peak amplitude lower than that of the individual waves, or could result in total destruction of the waves.
Waves that are constructively interfering with one another will produce an *interference maximum*, a bright spot, on an appropriately positioned and oriented detector. Looking at Figure 6.12, for the two waves to interfere constructively, the path length difference must be an integer number of wavelengths. For rays incoming at angle $\vartheta$, the path length difference $x$ can be defined as:

$$x = d \sin \vartheta + d \sin \vartheta$$  \hspace{1cm} (6.3)

For the path length difference to be equal to an integer $n$ number of wavelengths, $\lambda$, Bragg’s law can be defined as:

$$2d \sin \vartheta = n\lambda$$  \hspace{1cm} (6.4)

If the wavelength of the X-rays is known, the angle at which bright spots appear on the detector can be used to determine the distance between successive layers in the graphite crystal, $d$, as defined in Figure 1.4. By substituting the angle of a strong peak into Equation (6.4) the lattice spacing can be determined.

Two other important parameters that are used to define a crystal lattice are the $a$-spacing and $c$-spacing, as shown in Figure 1.4 and Figure 1.5. These parameters define the unit cell of the lattice, the simplest repeating structure that makes up the bulk material. The $a$-spacing defines the distance across the unit cell, while the $c$-spacing defines the height of the unit cell. Since graphite exhibits an ‘A – B – A – B’ repeating structure [8], the $c$-spacing is expected to be twice the value of $d$, the layer spacing.

Different crystal lattice structures exhibit different relationships between values of $a$, $c$ and $d$. Graphite exhibits a hexagonal lattice that is defined using [82]:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$  \hspace{1cm} (6.5)

where $h$, $k$ and $l$ are the Miller Indices corresponding to a specific peak, and $a$ and $c$ define the size of the unit cell. Hence to calculate the $a$-spacing and $c$-spacing, specific peaks must be considered. The $a$-spacing can be derived from the (110) peak,
since the term containing \( c \) in Equation (6.5) is set to zero by the value of \( l \). The \( c \)-spacing is derived from the (002) peak, which sets the value of \( h \) and \( k \) to zero. By selecting the appropriate peak from a diffraction pattern, determining the angle it appears at, and then calculating the \( d \)-spacing using Equation (6.4), the unit cell parameters can be calculated.

For powder samples, an alternate method of characterising crystalline materials exists. Known as Rietveld refinement, the techniques uses a least squares fitting technique to fit a theoretical profile to a measured profile. Parameters such as peak height and width, and preferential orientation of crystallites, can be determined using this technique. However, it was not used during this project since it is only applicable to powder samples.

When calculating the layer spacing and lattice parameters, there are a number of errors that reduce the overall accuracy of the results. These errors must be taken into account to assess the validity of the data. One of the major errors occurs due to uncertainty in the angle at which the various peaks in the diffraction pattern occur. The size of this error varies at different peak angles, as shown in Figure 6.13 below.

![Figure 6.13: Graph showing the angle of a peak plotted against the \( d_{002} \) spacing.](image)

The gradient of the curve in Figure 6.13 is greatest at low angles. Therefore, any error in the angle at which a peak occurs will result in a large error in calculated lattice
parameters, if the peak is at a low angle. If a peak at a large angle is used, the gradient is lower so the error on the lattice parameters will be smaller.

This can also be shown through differentiation of Bragg’s law:

\[ 2d \sin \theta = n\lambda \] (6.4)

\[ \frac{1}{d} = \frac{2 \sin \theta}{\lambda} \] (6.6)

\[ -\frac{\delta d}{d^2} = \frac{2\delta \theta \cos \theta}{\lambda} \] (6.7)

\[ -\frac{\delta d}{d} = \frac{\delta \theta}{\tan \theta} \] (6.8)

Since the tangent term nears infinity as the peak angle tends to 90°, the error associated with \( d \) gets smaller as the angle increases.

When quantifying the errors associated with \( d, c \) and \( a \) calculated from Equations (6.4) and (6.5), it is assumed that the wavelength of the X-rays is accurate. Hence the only variable that has an associated error is the peak angle, \( \theta \). The error associated with layer spacing parameter \( d \) is therefore:

\[ \frac{\sigma_d}{d} = \frac{\sigma_{(\sin \theta)^{-1}}}{(\sin \theta)^{-1}} \] (6.9)

\[ \sigma_d = d \sigma_{\theta} \cot \theta \] (6.10)

which is analogous to Equation (6.8).

To calculate the errors associated with the \( a \) and \( c \) parameters, Equation (6.5) must be simplified to remove terms that are not relevant for specific peaks. For \( a \)-spacing error calculation using the (110) peak:

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) = \frac{4}{a^2} \] (6.11)
X-Ray Crystallography Experiments

\[ a^2 = 4d^2 \quad (6.12) \]

\[ a = 2d \quad (6.13) \]

\[ \sigma_a = 2\sigma_d \quad (6.14) \]

The error associated with the c-spacing parameter can be derived using the (002) peak:

\[ \frac{1}{d^2} = \frac{l^2}{c^2} = \frac{4}{c^2} \quad (6.15) \]

\[ \sigma_c = 2\sigma_d \quad (6.16) \]

Initially, the values of \(a, c\) and \(d\) for Gilsocarbon, PGA-AG and PGA-WG samples were quantified at zero applied load using data from the diffraction spectra, as shown in Figure 6.2, Figure 6.3 and Figure 6.4. The (002) peak was used in conjunction with Equation (6.4) to calculate the \(d\)-spacing. Although using higher-order peaks would result in smaller errors as shown in Figure 6.13, the (002) is a strong, well defined peak and as such is most commonly used for layer spacing calculations in graphite. The (110) peak was used in conjunction with Equation (6.5) to calculate the value of the \(a\)-spacing, while the same equation was used in conjunction with the (002) peak to determine the c-spacing. The results are shown in Table 6.5.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Material</th>
<th>(a) [Å]</th>
<th>(c) [Å]</th>
<th>(d_{002}) [Å]</th>
<th>Unit cell volume [Å³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G008</td>
<td>Gilsocarbon</td>
<td>2.4615</td>
<td>6.7429</td>
<td>3.3719</td>
<td>35.282</td>
</tr>
<tr>
<td>G009</td>
<td>Gilsocarbon</td>
<td>2.4623</td>
<td>6.7438</td>
<td>3.3719</td>
<td>35.409</td>
</tr>
<tr>
<td>P007</td>
<td>PGA-WG</td>
<td>2.4628</td>
<td>6.7531</td>
<td>3.3765</td>
<td>35.472</td>
</tr>
<tr>
<td>P107</td>
<td>PGA-AG</td>
<td>2.4618</td>
<td>6.7437</td>
<td>3.3719</td>
<td>35.394</td>
</tr>
</tbody>
</table>

Table 6.5: Values of \(a, c, d_{002}\) and unit cell volume for Gilsocarbon, PGA-AG and PGA-WG samples at zero load.
There is significant agreement between the experimentally derived values of a, c and d and the values presented in the existing literature. As discussed in Section 1.3, previous studies have derived values of $a = 0.25$ nm, $c = 0.67$ nm and $d_{002} = 0.34$ nm. The results shown in Table 6.5 agree with these observations, with the small differences between the experimental data and the literature explained by the expected variations between different grades of graphite and the inhomogeneity between different samples from the same grades of graphite.

Having confirmed the properties of the crystal structure with no applied load, the stress-induced variation of this behaviour was studied by applying an axial prestress to the samples. Using the Deben Microtester, a different level of prestress was applied to each sample, the samples were scanned and values of $a$ and $c$ were determined from the diffraction spectra. It should be noted that since the X-ray diffraction was not being performed during in-situ application of stresses, only the residual stresses resulting from permanent sample deformation can be observed in this study.

These values were plotted in a series of graphs to show the effects that stresses have on the layer spacing and unit cell parameters. Figure 6.14 and Figure 6.15 show the relationship between the applied prestress and the values of $c$ and $a$ respectively for Gilsocarbon, PGA-AG and PGA-WG.

### 6.4.2.1 Unit Cell Parameters

Figure 6.14 shows the stress-induced variation of the c-spacing parameter with increasing prestress for Gilsocarbon, PGA-AG and PGA-WG samples, calculated using Equation (6.5) in conjunction with data from the diffraction spectra. As discussed in Section 1.3 and as shown in Figure 1.4, the $c$-direction is oriented perpendicular to the crystal lattice planes. The forces acting in the $c$-direction are the weak Van der Waals forces that hold the separate layers together, so it was expected that applying a compressive load would cause relatively large changes in the spacing between lattice planes. However, the magnitude of these changes was expected to depend strongly on the degree of anisotropy in the materials, and the orientation of the samples with respect to the applied loads.
Figure 6.14: Graph showing the relationship between applied stress and $c$-spacing for the Gilsocarbon, PGA-AG and PGA-WG samples.

The stress-induced variation of $c$-spacing occurred linearly for each of the three materials studied. The PGA-AG samples exhibited a linear reduction in the value of $c$ during the build-up of internal stresses. This suggests that adjacent layers in the crystal lattice were moving closer together as the applied load increased. This behaviour is reasonable since the load was applied perpendicular to the grain direction which, as discussed above, is also perpendicular to the lattice layers themselves. These weak bonds are relatively simple to break (compared to the forces required to deform other orientations of PGA), hence the samples were able to deform and shrink in the $c$-direction.

The opposite behaviour was observed for the PGA-WG sample. In previous chapters the reduced shrinkage of features in PGA-WG when compressed with the grain direction was attributed to the increased stiffness of the material. The bonds that have components acting parallel to the grains and lattice plains are strong and covalent, which suggests that less sample shrinkage would be observed along the loading axis.

Lastly, Gilsocarbon was observed to show a linear increase in $c$-spacing. Gilsocarbon exhibits no large scale directionality, despite exhibiting the same crystal
lattice structure as the PGA samples. The stiffness of Gilsocarbon has been shown to be similar in all directions. The linear increase in c-spacing shown in Figure 6.14 suggests that the crystal lattice layers moved further apart as the applied prestress was increased.

Figure 6.15 shows the stress-induced variation of α-spacing in Gilsocarbon, PGA-AG and PGA-WG samples, calculated using Equation (6.5) in conjunction with the diffraction spectra data. Since the α-direction is always perpendicular to the c-direction, it was expected that the behaviour of α-spacing under load would be the opposite of that for c-spacing.

![Graph showing the relationship between applied stress and α-spacing for the Gilsocarbon, PGA-AG and PGA-WG samples.](image)

The most obvious difference between the stress-induced variation of α-spacing and c-spacing is that the magnitude of the changes to the α-spacing is significantly smaller than that for the c-spacing. This observation is true for Gilsocarbon, PGA-AG and PGA-WG. The reason for these observations is the relative strengths of the forces that hold the crystal lattice together in different directions. Atoms are held together within each lattice layer by strong covalent bonds, while the layers themselves are held together by weak Van der Waals forces. To cause changes in the c-spacing, only the weak Van der Waals forces need to be overcome, while to change the α-spacing the
much stronger covalent forces need to be overcome. Therefore, the observed change in the \( a \)-spacing per unit applied load is significantly smaller than the change in \( c \)-spacing per unit load.

In the PGA-AG samples, the \( a \)-spacing was found to increase linearly as the applied load increased. This suggests that when the sample is compressed perpendicular to the \( a \)-direction, the crystal lattice expands in the \( a \)-direction. This behaviour is the opposite of what was observed when studying the \( c \)-spacing, so the results agree with the predictions. After the removal of the load, the deformation will not fully recover, resulting in a small amount of permanent dimensional change.

The PGA-WG sample exhibited a linear decrease in \( a \)-spacing, which suggests that unit cell shrinkage is occurring parallel to the loading direction. This behaviour was expected, and was opposite to the behaviour of \( a \)-spacing in PGA graphite when compressed perpendicular to the loading axis. Once again, the rate of change of \( a \)-spacing of PGA-WG was observed to be smaller than the \( a \)-spacing change in PGA-AG.

The observed rate of change for Gilsocarbon was smaller than that observed in both PGA-WG and PGA-AG. A linear increase in \( a \)-spacing with increasing load was observed. This result was unexpected, since it represents the only instance where the same behaviour under load was observed for both \( c \)-spacing and \( a \)-spacing. In both orientations of PGA, either \( c \) increases and \( a \) decreases, or vice versa. However, applying a compressive load to the Gilsocarbon samples resulted in an increase in both \( c \) and \( a \). These observations suggest that the unit cell in Gilsocarbon is shrinking in all directions when an axial load is applied.

### 6.4.3 Lattice Strain and Crystallite Size

When examining loaded samples, it is possible to determine whether the strain is uniform or non-uniform based upon the behaviour of peaks in the diffraction pattern. For a given peak, the growth of uniform strain will result in a shift in the angle at which the peak appears. If the strain is non-uniform, the peak width will change.

These rules can be used to gain an approximation of the strains in a sample during X-ray diffraction. However, a more accurate method of quantifying this behaviour was defined by Williamson and Hall [84]. In a technique known as the
‘Williamson-Hall’ method, strains can be calculated from a diffraction pattern. Equation (6.17) and Equation (6.18) show how size broadening, $\beta_L$, and strain broadening, $\beta_E$, vary differently with respect to the Bragg angle $\theta$:

$$\beta_L = \frac{K\lambda}{L_{h,k,l} \cos \theta}$$  \hspace{1cm} (6.17)

where $L_{h,k,l}$ is the lattice parameter, $K$ is a shape factor and $\lambda$ is the wavelength of the X-rays used. The shape factor is a value that is affected by the shape of the crystallite but is independent of its dimensions. Traditionally it was treated as a constant, often being assigned a value of 1 [10], but more recent studies have shown that it is a function of crystallite size [85].

For this study the shape values were defined as 0.9 for $L_c$ [85, 86] and 1.84 for $L_a$ [85, 86], with these values selected by studying the existing literature. The average layer diameter $L_a$ is typically calculated using the (110) peak, while layer thickness $L_c$ is measured from the (002) peak. These peaks are the same as those used for calculation of unit cell parameters in Section 6.4.2.

Strain broadening, $\beta_E$, can be calculated using Equation (6.18):

$$\beta_E = C\epsilon' \tan \theta$$  \hspace{1cm} (6.18)

where $C$ is a constant and $\epsilon'$ is the mean inhomogeneous strain.

Therefore, total line broadening, $\beta_{tot}$, can be calculated using:

$$\beta_{tot} = \beta_L + \beta_E = \frac{K\lambda}{L_{h,k,l} \cos \theta} + C\epsilon \tan \theta$$  \hspace{1cm} (6.19)

Multiplying by $\cos \theta$:

$$\beta_{tot} \cos \theta = C\epsilon' \sin \theta + \frac{K\lambda}{L_{h,k,l}}$$  \hspace{1cm} (6.20)

Equation (6.20) takes the form of the standard equation of a line:
where \( m \) is the gradient of the line and \( c \) is the value where the line crosses the \( y \)-axis. Therefore, by plotting \( \beta_{\text{tot}} \cos \theta \) against \( \sin \theta \), the strain component and size component can be read from the graph, as shown in Figure 6.16 below. This type of graph is known as a ‘Williamson-Hall plot’.

For each individual peak in a diffraction pattern, the full width half maximum width and the angle at which the peak occurred was calculated, and a graph of \( \beta_{\text{tot}} \cos \theta \) against \( \sin \theta \) was plotted, similar to Figure 6.16. The gradient of this graph is proportional to the mean inhomogeneous strain. By repeating these calculations using samples that have been exposed to a range of compressive stresses, the rate of growth of internal strains can be studied.

It is important to note that peak broadening can also be an artefact of the diffractometer, and should be taken into account when using the Williamson-Hall method. These artefacts have a number of causes, including misalignment of the diffractometer, axial divergence of the beams and suboptimal configuration of slits.
used in the diffractometer. Instrumental contributions to peak broadening can be calculated by performing X-ray diffraction analysis on a near-perfect sample known to exhibit negligible peak broadening. Any deviation from the expected values is assumed to be caused by instrumental broadening.

Figure 6.17 shows the Williamson-Hall plot for the PGA-AG samples. For each sample five peaks were defined in the diffraction pattern, hence five data points were plotted on the graph.

![Williamson-Hall plot](image)

**Figure 6.17**: Williamson-Hall plot for the PGA-AG samples at a range of different loads. Best-fitting lines are not shown to ensure the data points themselves are clear, and are quantified in Figure 6.20 instead.

Looking at the data in Figure 6.17, it appears that there is a linear trend between the values of \( \sin \theta \) and \( \beta \cos \theta \). The linear trend allowed the strain component of Equation (6.20) to be calculated using the gradient of the best-fitting line. The behaviour of the data was similar to that shown in Figure 6.16, with the exception that the data points derived from the (110) peak (i.e. the fifth data point in each series) were lower than expected. This suggests that the width of the (110) peaks were not as wide as anticipated. However, each data series can still be well described using a linear best-fitting trend line, which means that the strain within each sample can be quantified using the Williamson-Hall method.
The best-fitting lines for each sample are not shown in Figure 6.17 due to them obscuring the data points too much, due to the close proximity of the points to one another and the large amount of data shown in the graph. Instead, the gradients of the best-fitting curves are plotted against the load applied to each sample in Figure 6.20, and shall be discussed later.

The above analyses were repeated for the PGA-WG and Gilsocarbon samples, for which the Williamson-Hall plots are shown in Figure 6.18 and Figure 6.19 respectively.

Figure 6.18: Williamson-Hall plot for the PGA-WG samples at a range of different loads. Best-fitting lines are not shown to ensure the data points themselves are clear, and are quantified in Figure 6.20 instead.

Figure 6.18 shows that the PGA-WG samples exhibit similar behaviour to the PGA-AG samples. A positive linear correlation between $\sin \theta$ and $\beta \cos \theta$ was observed, and the values of $\beta \cos \theta$ were lower than anticipated for the (110) peaks from each sample. The gradients of the best fitting lines for each sample were calculated, and are shown in Figure 6.20.
Figure 6.19: Williamson-Hall plot for the Gilsocarbon samples at a range of different loads. Best-fitting lines are not shown to ensure the data points themselves are clear, and are quantified in Figure 6.20 instead.

Figure 6.19 shows the Williamson-Hall plot for the Gilsocarbon samples. A positive linear correlation between $\sin \theta$ and $\beta \cos \theta$ was observed. The values of $\beta \cos \theta$ were once again lower than anticipated for the (110) peaks from each sample, but not as low as the (110) peak in the PGA-WG sample.

As discussed above, the best-fitting lines are not shown on Figure 6.17, Figure 6.18 or Figure 6.19 since the obscure the data points too much. Instead, the gradient of the best-fitting line for each sample has been calculated and as plotted against the load applied to each sample, as shown in Figure 6.20.
Figure 6.20: Graph showing the gradient of each best-fitting line plotted against the applied load for each sample. The value of each point is proportional to the mean inhomogeneous strain.

Figure 6.16 shows that the gradient of the Williamson-Hall plot is equal to the product of the mean homogeneous strain and a constant. Although the value of the mean homogeneous strain cannot be calculated itself, the gradients of the lines in Figure 6.20 are directly proportional to the mean homogeneous strains and, more importantly, the stress-induced changes to this parameter can be observed.

The data in Figure 6.20 suggests that the load applied to each sample has a significant effect on the mean inhomogeneous strain within each sample. For the PGA-AG and PGA-WG samples, increasing the level of applied prestress resulted in a linear decrease in the gradient of the best-fitting lines, and hence a linear decrease in the mean inhomogeneous strain within the sample. Conversely, the Gilsocarbon samples exhibited a linear increase in mean inhomogeneous strain as the applied prestress increased. The rate of change was greatest for the PGA-WG samples, followed by the Gilsocarbon samples, and smallest for the PGA-AG samples.

The difference in behaviour of the Gilsocarbon samples and the PGA samples was unexpected. One possible explanation for these observations relates to the ability of the materials to recover when applied loads are removed. The preliminary stress-strain relationship studies in Section 4.3 showed that both Gilsocarbon and PGA exhibit
partial sample recovery once any applied compressive loads are removed. Since the samples here are prestressed prior to undergoing X-ray diffraction, the only microstructural changes that are being observed in Figure 6.20 are residual stresses and non-recoverable deformation that was caused during loading.

Bodel [46] performed a series of qualitative confocal microscopy studies on Gilsocarbon and PGA graphite. He observed that the response of the filler particles to the release of any applied compressive loads was different in Gilsocarbon and PGA. Gilsocarbon’s spherical filler particles exhibited a much greater tendency to show significant recovery from all but the highest loads (typically within a few percent of sample failure). By comparison, filler particles in PGA showed a much lower tendency for recover, cracking and irreversibly deforming at lower loads.

The ability of filler particles in Gilsocarbon to partially recover from loads that would permanently damage PGA filler particles may explain the behaviour of the samples shown in Figure 6.20. The filler particles in Gilsocarbon are able to remain intact during stress application and the associated build-up of strains, which results in an increase in mean inhomogeneous strain as shown in Figure 6.20. The PGA filler particles, however, respond to stress growth by cracking, relieving the strains and stopping them from building up.

This does not explain why the behaviour of the PGA-AG and PGA-WG samples are so similar. Throughout the project PGA-WG samples have been shown to be stiffer and more resistant to dimensional change than PGA-AG samples, so it is not clear why this well-established behaviour is not apparent here.

An alternate explanation of this behaviour is that the loading process is relieving strains stored in the PGA samples during the manufacturing process.

6.4.3.1 Crystallite Size

As shown in Figure 6.16, the point at which the best-fitting line crosses the y-axis can be used to determine the crystallite size of the material. Crystallite size $L$ can be determined from the shape factor of the sample, $K$, the wavelength of the X-rays used, $\lambda$, and the value of the y-intercept of the best-fitting line, $y$, as shown in Equation (6.22):
Figure 6.21 shows the values of the gradients of each of the best-fitting lines used to calculate the crystallite sizes of the graphite samples.

The data from Figure 6.21 were used in conjunction with Equation (6.22) to calculate values of crystallite size for each sample at a range of loads, as shown in Figure 6.22.
Figure 6.22: Values of crystallite size for each sample at a range of applied loads.

The values of crystallite size shown in Figure 6.22 show variable amounts of loading-induced change, with the amounts of change depending on the material and orientation being studied. Both Gilsocarbon and PGA-WG exhibited a reduction in the crystallite size when the applied load increased, while PGA-AG exhibited an increase in the crystallite size during loading. The opposite behaviour of the two PGA samples was expected since similar behaviour was observed when studying stress-induced variation of \(\alpha\)-spacing and \(c\)-spacing parameters. In this case, Gilsocarbon appears to follow the same trend at PGA-WG, with a small loading-induced reduction in crystallite size.

### 6.4.4 Bacon Anisotropy Factor

The Bacon Anisotropy Factor (BAF) is a quantitative measure of the degree of preferential orientation of lattice planes in a material [88]. It can be calculated using Equation (6.23) [89]:

\[
B.A.F. = \frac{\int_0^{\pi/2} I(\varphi) \cos^2 \varphi \, d\varphi}{\int_0^{\pi/2} I(\varphi) \cos^3 \varphi \, d\varphi}
\]  

(6.23)
where $I(\varphi)$ is the density of the (002) plane normals per unit solid angle about angle $\varphi$, and angle $\varphi$ represents the angle between the (002) pole of the crystallites with respect to the normal of the deposition plane [89].

An approximation of the Bacon Anisotropy Factor can be calculated using Equation (6.24) below:

$$B.A.F. = \frac{h(002)_{AG}}{h(002)_{WG}}$$

(6.24)

where $h$ represents the height of a specific diffraction pattern peak, after removing the background counts, and $AG$ and $WG$ represent the against-grain and with-grain sample orientations respectively.

Values of the Bacon Anisotropy Factor can provide useful insight into the degree of anisotropy within a material. As discussed in Section 1.5.1, PGA graphite is known to be highly anisotropic and, throughout this project, measurements of PGA’s properties have been made perpendicular and parallel to the grain direction. This was continued with the X-ray diffraction experiments, enabling calculation of the BAF for each PGA sample. Gilsocarbon is known to be quasi-isotropic, and previous experiments into the material have showed little anisotropy. Intuitively, one would expect a greater BAF value for PGA graphite than Gilsocarbon graphite. However, since the results of the pore orientation study in Section 4.8.3 observed a small degree of anisotropy at a small range of angles, it was decided that the Gilsocarbon samples would be measured at a range of orientations. It was anticipated that the results of this study would correlate with the observations during the pore orientation study and confirm that the Gilsocarbon samples have a small degree of anisotropy.

Using the X-ray diffraction spectra produced for each sample, the height of the (002) peaks were calculated for each sample, and the ratios of appropriately-oriented values were calculated to determine the degree of anisotropy in each case. These results were then compared to the existing literature to determine how representative the samples, and the graphite blocks they were machined from, are of the bulk material.
Figure 6.23 shows values of the Bacon Anisotropy Factor for Gilsocarbon and PGA calculated at a range of applied loads.

![Graph showing variation of Bacon Anisotropy Factor](image)

Figure 6.23: Variation of the Bacon Anisotropy Factor in Gilsocarbon and PGA graphite at a range of applied loads.

At zero load, the Bacon Anisotropy Factor of PGA was shown to be 2.18, while the value for Gilsocarbon was 1.13. This shows that PGA is highly anisotropic, while Gilsocarbon exhibits a small degree of anisotropy. Both of these values were expected. The ordering of the filler particles in PGA give the material different properties depending on the orientation being considered, and the relatively large BAF emphasises the degree of anisotropy present in the material. Gilsocarbon is manufactured to be quasi-isotropic, and the pore orientation studies in Section 4.8.3 identified a small degree of preferential orientation within the pores, which suggested that the BAF would be greater than one, but still smaller than the value for PGA. Figure 6.23 shows that the BAF at zero load in Gilsocarbon is 1.13, which is indicative of a small amount of anisotropy.

Applying a compressive prestress to the PGA samples and measuring the BAFs resulted in a linear increase being observed. As the applied load was increased to 900 N, the value of the BAF increased by 18.3%. This indicates that the PGA samples become more anisotropic as the level of prestress increases.
When a compressive prestress was applied to the Gilsocarbon samples, a linear increase in BAF was observed, but the rate of change per unit applied load was approximately six times smaller than that for PGA. As the prestress was increased to 600 N, the value of BAF increased by 6.2%. This indicates that, like PGA, Gilsocarbon becomes more anisotropic as the level of prestress increases. The smaller rate of change in Gilsocarbon is governed by the material’s greater stiffness and resistance to dimensional change compared to PGA.

6.5 Conclusions

The X-ray diffraction studies have allowed significant insight to be gained into how the crystal structure of graphite responds to the development of stresses. Measurements of layer spacing, unit cell parameters, crystallite sizes, lattice strains and degrees of anisotropy were performed on prestressed samples of Gilsocarbon and PGA. Although the experiments were limited by the inability to collect in-situ data during the application of compressive loads, the observations discussed in this chapter extend beyond the existing literature in this field.

After measurement of main crystallite parameters $a$, $c$ and $d$, it was found that the behaviour differed for PGA-AG and PGA-WG. For example, applying a compressive load to the PGA-AG samples increased the value of the $a$-spacing, but this value decreased when the PGA-WG samples. This behaviour was adequately explained by the strengths of the forces holding the atoms and lattice planes together. The Gilsocarbon samples exhibited unexpected behaviour whereby values of $a$, $c$ and $d$ all increased as the applied prestress increased.

The Williamson-Hall method was used to quantify the build-up of strains and calculate the crystallite sizes of the samples. It was found that the inhomogeneous strain in Gilsocarbon and PGA exhibited opposite behaviours when the applied prestress was increased, and a possible explanation for these observations relating to the deformation of filler particles was made.

Lastly, a study of the degree of anisotropy in PGA and Gilsocarbon showed that both grades of graphite became more anisotropic as the level of prestress was increased.
The experiments investigating the variation of the crystal lattice have yielded valuable information regarding the response of the material to stresses. Even though the experiments were limited to the study of residual stresses, as opposed to the in-situ stress generation techniques utilised in the rest of this project, the observations made at this level will help explain the observations made at larger length scales. Since it is the behaviour at the atomic level that ultimately underpins the bulk behaviour of the material, the findings in this chapter provides novel and useful data on how graphite responds to stress at the atomic level.

As has been discussed extensively in this chapter, the main limitation of these X-ray diffraction studies is that the experiments were investigating the effects of residual stresses as opposed to in-situ stresses. As discussed in Section 4.3, graphite can partially recover from stress-induced deformation, hence only non-recoverable damage was observed in the X-ray diffraction experiments. Non-recoverable damage has been shown to be small compared to the recoverable damage caused by axial loading in PGA and Gilsocarbon.

None of the X-ray diffractometers available at the University of Manchester’s X-ray diffraction suite in the School of Materials have the capability to produce diffraction patterns for sample during the application of a compressive load. This means that in order to collect in-situ data on stress-induced crystal structure variation, a new rig will have to be manufactured. It will be difficult to build a rig compatible with the available machines due to the size and weight limitations of the machines.

However, there is a diffractometer compatible with compression rigs that can perform a limited form of X-ray diffraction. The Proto Residual Stress Diffractometer (PRSD) uses an X-ray source and detector mounted on a robotic arm, enabling free movement around a fixed sample, and the same stage is large enough for the use of in-situ sample environments. However, the system is incapable of producing full diffraction spectra, and instead can focus only specific angles as opposed to a continuous series of angles. This limits the types of observations that can be made about a material’s crystal structure, but the ability to acquire in-situ data may prove useful. Performing in-situ experiments on graphite samples using the Proto Residual Stress Diffractometer may be an interesting topic for future X-ray diffraction studies.
6.6 Summary

- A series of X-ray diffraction experiments were performed on prestressed samples to determine how the crystal structure varies during stress growth. Diffraction spectra were analysed to acquire quantitative data regarding various properties of the crystal lattice.

- The Miller Indices of the Gilsocarbon and PGA samples were confirmed by comparing the X-ray diffraction patterns to data in the ICDD PDF-4 database.

- The \( d, a \) and \( c \) parameter values were calculated for Gilsocarbon, PGA-AG and PGA-WG initially with no applied load, and the values agreed with the existing literature.

- Generating stresses within the samples was found to change the values of the \( d, a \) and \( c \) parameters, with the variation depending on sample orientation. In each PGA sample \( d \) and \( c \) behaved similarly, while \( a \) behaved in the opposite manner. In Gilsocarbon the \( d, a \) and \( c \) parameters all increased with the applied load.

- Stress-induced variation of lattice strains was quantified, with PGA-AG and PGA-WG exhibiting a decrease in mean inhomogeneous strain, while Gilsocarbon exhibited an increase in mean inhomogeneous strain. A possible explanation for this behaviour relating to the closure and recovery of filler particles was proposed.

- Crystallite size was also found to vary with the applied load. PGA samples exhibited opposite changes of crystallite size when a compressive load was applied, while Gilsocarbon’s behaviour was similar to that of the PGA-WG sample.

- Both Gilsocarbon and PGA exhibited a loading-induced increase in Bacon Anisotropy Factor. PGA was observed to be highly anisotropic, while only a small degree of anisotropy was observed in Gilsocarbon. The rate of change of BAF per unit load was six times greater in PGA than in Gilsocarbon.

- The limitations of not being able to collect in-situ data during this study were discussed. An in-situ experiment was proposed for future work. A proposal was made for further experiments, albeit experiments of limited scope, using the Proto Residual Stress Diffractometer.
Chapter 7: Concluding Remarks

This chapter summarises the work discussed in the earlier chapters, analysing the results and defining the significant new observations, interpretations and insights that have arisen from this project. In depth conclusions on each individual experimental technique have been included at the end of each of the three main experimental chapters. This chapter summarises these conclusions, compares and contrasts the observations from the different experimental methods, and discusses the observations in the context of the existing literature and the current understanding of stress-induced graphite deformation behaviour. The project is then discussed in the context of the graphite-moderated nuclear reactor industry, in order to evaluate the relevance and usefulness of the data collected. Finally, a series of suggestions for future experimental work and analyses, to extend or enhance this project, have been made.

7.1 Conclusions

The aim of this project was to investigate how stresses affect the material and microstructural properties of nuclear grade graphite used in British graphite-moderated nuclear reactors. With many of Britain’s graphite-moderated reactors aging and undergoing life extension, in order to maintain safe operational parameters, it is important to have a detailed understanding of how graphite components degrade during operation. Since the graphite bricks cannot be replaced or repaired, their structural integrity is a limiting factor on the operational lifespan of the reactor. There is considerable pressure on the British nuclear industry to keep these reactors operational and providing energy to the National Grid, but the safe operation of the reactors is paramount. The cracking and degradation of graphite reactor components is uncharted territory, necessitating a considerable amount of research into the behaviour of graphite components over time and the safe operational lifetimes of Britain’s graphite-moderated reactor fleet.

With that in mind, an experimental programme was proposed to investigate the stress-induced variation of the pore structure and Young’s modulus of various grades of graphite. Graphite is a highly porous material and growth of the pore structure is a significant contributor to the stress-induced degradation and eventual cracking of graphite bricks, while Young’s modulus is a measure of stiffness of a
material and is related to the stress it experiences. These topics were selected for study following a comprehensive literature review of deformation behaviour in nuclear graphite, during which significant gaps and flaws in our understanding of the behaviour of porosity and the crystal structure over time in nuclear reactors were identified.

Three experimental techniques were selected to gain insight into the stress-induced deformation behaviour of graphite – the imaging techniques of confocal laser microscopy and X-ray tomography, and the crystal lattice analytical technique of X-ray diffraction.

The first series of experiments were performed using confocal laser microscopy. Confocal microscopy allowed two-dimensional studies of the behaviour of graphite to be made. Compared to traditional optical microscopy, the ability of a confocal microscope to produce images with depth selectivity (i.e. ‘2.5D’ images) resulted in the acquisition of higher quality data, although still not as insightful as fully three-dimensional data.

An axial compression rig was used to simulate the stresses that would be experienced by graphite components in working nuclear reactors. Images were recorded at a range of applied loads, allowing the deformation of the pore structure to be observed in real-time. Pore areas, eccentricities, orientation angles, angularity and separation were measured for a range of applied loads, enabling the stress-induced variation of porosity to be understood in great detail.

Pore areas were found to decrease linearly as the applied load increased, while the pores themselves were observed to become more eccentric. A small amount of clockwise rotation of pores with respect to the loading axis was observed, and it was proposed that pore shrinkage and pore rotation were competing processes. The mean measure of angularity of the pores in each sample was found to decrease linearly in materials with pore ordering parallel to the loading axis, and increase in materials with pores oriented perpendicular to the loading axis. Changes to the binder and filler phases were quantified using a nearest neighbour study and a Voronoi study. These techniques were selected to eliminate the effects of pore shrinkage on the results.

For each of the above properties, a clear relationship was observed between the property itself and the applied load. The strength of the correlation varied, but the variation of each property was found to be dependent upon the level of compressive load applied, and affected by any preferential directionality of pores and filler particles.
within the material. For each observed relationship, an explanation for the behaviour was proposed.

The existing research into stress-induced deformation behaviour of graphite is somewhat limited. As discussed in Chapter 2, much of the relevant studies are either qualitative in nature, limited to the study of pre-stresses, or focussed on the bulk material. Therefore the confocal microscopy studies presented in Chapter 4 represent a significant advance over existing research. The ability to acquire in-situ data on the deformation behaviour of graphite, and quantitatively study this behaviour at the microlevel, has yielded significant contributions to knowledge in this field.

Additionally, many of the techniques used to analyse the data were novel, with the intention of refining existing techniques, and finding new ways to study previously unstudied phenomena. For example, while observations of pore eccentricity at zero load have been performed by Kane [56], a new method was created in Section 4.8.2 to eliminate poorly fitting ellipses prior to eccentricity analysis, which significantly improves the validity of the conclusions made from the data. The subsequent analysis of pore eccentricity at varying loads has not been performed previously for nuclear grade graphite. Another example occurs during the pore orientation analysis in Section 4.8.3, where a novel hypothesis regarding the conflict between pore collapse and pore rotation was proposed, based upon the observed results. A summary of the main novel techniques and contributions to our understanding of this field is provided in Section 4.11.

Although the confocal microscopy experiments were successful and a large amount of useful data was acquired, the limitations of two-dimensional studies were a concern. Therefore, it was decided that the next series of experiments would require a fully three-dimensional image acquisition technique.

The second series of experiments were performed using X-ray tomography. X-ray tomography allowed three-dimensional studies of graphite behaviour to be made, which represented a significant improvement over two-dimensional studies. During the literature review the limitations of performing two-dimensional studies of three-dimensional phenomena were noted, so X-ray tomography was expected to provide the most useful and reliable data for the imaging section of the project.

Once again an axial compression rig was used to stress the samples to a range of loads during acquisition of tomography images. The tomography data were
reconstructed and a fully three-dimensional representation of the microstructure of the sample was used to study the behaviour of the pore structure. Pore volumes, surface areas, eccentricities and angularities were measured at a range of applied loads. For each of these properties, a clear relationship was observed between the property itself and the applied load, and explanations for the relationships were proposed.

As with the confocal laser microscopy results, many of the observations were either novel in themselves, or utilised a novel method of acquiring or analysing the data. For example, the novel technique for excluding poorly-defined ellipses from the eccentricity study created in Section 4.8.2 was extended to three dimensions, while the error introduced by image thresholding was calculated using a new and precise method. The refinement of existing techniques, creation of new techniques and acquisition of novel data presented in Chapter 5 emphasise the useful contributions this study has made to the understanding of the microstructural response to stress of graphite. A summary of the main novel techniques and contributions to our understanding of this field is provided in Section 5.9.

For each pore property studied, the confocal microscopy and tomography results were compared to determine the correlation existing between the two-dimensional and three-dimensional results. Significant agreement between the two sets of data would suggest that both methods are equally applicable, while disagreement would imply that two-dimensional techniques are unsuitable for studying three-dimensional data.

Overall, no conclusive trend was observed. For properties such as pore eccentricity, the results were remarkably similar for the two-dimensional method and the three-dimensional method. This shows that even though variation of pore eccentricity is a three-dimensional property, two-dimensional studies (such as traditional microscopy) can yield valid data in this behaviour. Conversely, studies of pore angularity results in significantly different behaviour using confocal microscopy and tomography techniques. This suggests that angularity cannot successfully be analysed to a high degree of precision with anything other than fully three-dimensional techniques. Other studies fell between these two extremes. For example, a numerical relationship between two-dimensional pore area data and three-dimensional pore volume data was observed. This suggests that two-dimensional pore areas are a
parameter that is useful for the deformation analysis of pores, even though pore deformation occurs three-dimensionally.

Given that two-dimensional analyses are easier to perform, available for a higher number of parameters and are historically more common than three-dimensional analyses, it is reassuring to see that in many cases these studies can be relevant and insightful, and are not rendered obsolete by the availability of three-dimensional data. While techniques such as X-ray tomography offer an undeniable advantage over their two-dimensional analogues, both techniques remain relevant for the acquisition of novel data regarding the deformation behaviour of graphite. However, it appears likely that three-dimensional techniques will provide the majority of high quality, novel data in the imaging field for the foreseeable future.

The third series of experiments were performed using X-ray diffraction. By projecting X-rays onto a graphite sample and studying the diffraction spectra produced by the X-rays as they diffract off the surface layers of the sample, information regarding the material’s crystal lattice can be acquired. Unlike the imaging studies, it was not possible to perform X-ray diffraction experiments in-situ, and the limitations that this caused have been discussed in detail.

As anticipated, the behaviour of the $c$, $d_{002}$ and $a$ parameters in PGA depended upon the orientation with respect to the loading direction. In each case applying a compressive load reduced the crystallographic parameters oriented parallel to the loading direction, while the parameters oriented perpendicular to the loading direction increased, but by a smaller magnitude. The same behaviour occurred with the crystallite size parameters $L_a$ and $L_c$, with one of the two parameters increasing and the other decreasing depending upon the orientation of the sample with respect to the loading direction.

The behaviour of the Gilsocarbon samples, however, was unexpected. As the applied prestress increased, the value of the $c$, $d_{002}$ and $a$ parameters all increased, which suggests the entire sample was expanding. Similar behaviour was also observed for the crystallite size parameters. It was noted that the Gilsocarbon sample exhibited the smallest changes in layer spacing, unit cell and crystallite sizes. In some cases the observed increases were very small and, more importantly, smaller than the magnitude of the errors associated with the parameters.
Subsequent experiments investigated the build-up of strains in the crystal lattice and quantified the degree of anisotropy in Gilscarbon and PGA. When studying the mean inhomogeneous strain within the samples at a range of applied prestresses, PGA-AG and PGA-WG were found to exhibit similar trends, while Gilscarbon exhibited the opposite behaviour to the PGA samples. PGA was found to be highly anisotropic, while only a small degree of anisotropy was observed in Gilscarbon. Both Gilscarbon and PGA exhibited a loading-induced increase in Bacon Anisotropy Factor, which indicates that applying a compressive load to the material makes it more anisotropic.

While the X-ray diffraction experiments resulted in the acquisition of novel data and enabled the response of the crystal lattice to stress to be studied, this section of the project is limited by the lack of in-situ data. Unlike the confocal laser microscopy and X-ray tomography studies, the X-ray diffractometer lacked compatibility with any in-situ sample stages, hence the experiments were limited to prestresses only. The results from this study are therefore not as useful as if the study were performed during the application of the compressive loads.

7.2 Further Work

The limitations of the experiments and analyses performed during the completion of this project have been discussed in considerable detail. Many of these limitations could be overcome by performing further experiments. These experiments could be specifically designed to counteract the limitations with the existing experiments.

However, it is also important to consider the limitation of time. Due to the limited amount of time available for the project, not all of the analyses that could be performed have been completed. More results and insight could be gained by performing further analyses on the data that has already been collected. Therefore, the further work that could be performed to continue this research can be split into two categories – additional analysis of existing data, and novel experimental and analytical work.
7.2.1 Further Analyses of Existing Data

During the confocal microscopy and tomography analyses of pore behaviour, a number of important pore parameters were selected for study, including pore volumes, orientations, angularity and spacing. These represent only a small number of the parameters that could be investigated. Other useful properties that were considered for study but ultimately rejected (for a range of reasons including lack of time and low importance compared to other parameters) include pore texture (as defined in Figure 4.34) and values of Feret’s diameter [90] parallel and perpendicular to the extrusion direction (where applicable). In addition, finding methods to extend the analyses performed using confocal microscopy data to fully three-dimensional tomography data, such as the pore orientation study, would yield further novel data. It would also allow additional comparisons to be made between two-dimensional and three-dimensional techniques, and would enable further analysis of the usefulness and relevance of 2D and ‘2.5D’ techniques.

The inhomogeneous stress distributions within axially compressed samples shown in Figure 4.44 were investigated briefly in Section 5.6.1.1, and investigation of this behaviour was identified as a suitable topic for further work. Mean pore area was found to vary based upon sample height, which was expected due to the inhomogeneous stress distributions within the samples, but pore orientation did not appear to be affected by this phenomenon. Performing studies of other pore parameters at different heights within each sample may yield useful information into how graphite components respond to stresses.

Stereology, the technique of extracting quantitative information about a three-dimensional object from two-dimensional data, as discussed in Section 2.4.2, was not used during the project. Direct comparisons of pore properties measured in two and three dimensions, such as pore eccentricity, were performed using the confocal laser microscopy data and X-ray tomography data, and performing stereology on the confocal laser microscopy data would allow further comparisons to be made with the X-ray tomography data.
7.2.2 Further Experimental and Analytical Work

Chapters 4 and 5 documented the acquisition of a large amount of data regarding the stress-induced variation of the pore structure in PGA and Gilsocarbon. For a range of pore properties such as pore volume, orientation, eccentricity, angularity and separation, the stress-induced variation of these properties were studied and detailed relationships between each property and the applied load were observed. These results could be used to produce a model of the pore structure in graphite for use in finite element modelling experiments.

Scanning electron microscopy and polarised light microscopy were identified as techniques that would provide suitable data, but were ultimately rejected, as discussed in Section 2.4.2. Further studies into the stress-induced deformation behaviour of graphite could be performed using these techniques. Scanning electron microscopy would enable high resolution images of graphite to be acquired; at length scales much smaller than the techniques utilised in this project have allowed so far. Polarised light microscopy allows different components of the graphite samples to be highlighted, and the high contrast and resolution of the technique make it well suited for the study of graphite.

Many detailed models of graphite bricks have been produced using software such as Abaqus, with the intention of simulating the conditions of a working reactor to study the behaviour of graphite components. The results of the confocal microscopy and tomography experiments discussed in Chapters 4 and 5 provide information regarding pore structure properties at zero load, and when exposed to a range of loads. These results can be used as inputs for models of graphite components. A wide range of models of graphite components exist, with the sizes and level of detail varying considerably. The inclusion of porosity in a model would improve the usefulness and relevance of the model to the real-life environment in which the graphite bricks operate. The comprehensive data on the pore structures of PGA and Gilsocarbon collected in this project would be ideal for use as numerical inputs for such a model.

In Section 5.7 it was concluded that three-dimensional imaging techniques have such significant advantages over two-dimensional techniques that the most useful and, in the future, novel experimental data was expected to come from three-dimensional studies. However, one of the main limitations of this study is that the X-ray tomography
was at a lower resolution than the confocal microscopy data. A pixel size of 2.5 µm was attained using the confocal microscope, but a pixel size of only 18 µm could be attained from the tomography experiments, mainly due to the size of the compression rig using in the tomography experiments. Figure 5.10 and Figure 5.11 show the range of pore sizes in Gilsocarbon and PGA graphite, and the power law relationship shows the strong bias towards small pores, emphasising the importance of achieving as high a resolution as possible when studying pore behaviour.

Performing similar tomography experiments at a higher resolution would allow a more accurate picture of the pore distribution and deformation behaviour to be attained. The use of a smaller deformation rig specifically designed to maximise the geometric magnification (as discussed in Section 5.1.1), such as that utilised by Kareh et al. [62], would improve the resolution of the images. Alternatively, performing imaging experiments without an in-situ sample environment would make acquisition of high resolution data much easier.

The limitations to the X-ray diffraction studies due to the inability to record diffraction spectra during compressive loading have been discussed in detail. However, as discussed in Section 6.5, the Proto Residual Stress Diffractometer at the University of Manchester is compatible with most in-situ sample environments, and could be used to perform X-ray diffraction during compressive loading of samples. However, this technique is limited and is not as versatile as the techniques discussed in Chapter 6.

The X-ray diffraction studies could also be extended by performing X-ray texture goniometry to determine the preferred orientation of the crystallites within the graphite samples. Graphical representations known as pole figures are used to show orientations of objects in the form of stereographic projections. This technique is well established in studies of nuclear grade graphites [91].

Another possible suggestion for future work would involve extending the established experimental techniques for the study of different grades of graphite. The grades of graphite selected for study in this project, Gilsocarbon and Pile Grade A, were chosen due to their use in current generation nuclear reactors in the UK. Candidate moderating materials for next generation graphite-moderated reactors, such as pebble-bed and prismatic block VHTRs, include other types of graphite not previously studied, and the microstructures of the grades of graphite are in some cases significantly different to Gilsocarbon and PGA. In particular, Gilsocarbon and PGA are
both relatively coarse grained grades of graphite, so a study of finer grained grades of graphite will probably result in significantly different behaviour being observed.

7.3 Summary

- A project was proposed to investigate stress-induced variation of the pore structure of various grades of graphite, to gain an insight into how graphite moderator components degrade in nuclear reactors.

- Confocal microscopy and tomography techniques were used to acquire two- and three-dimensional images of the pore structure during the in-situ application of compressive loads, while X-ray crystallography was used to study changes to the crystal structure.

- Variation of pore properties such as volume, surface area, eccentricity and orientation were studied using confocal laser microscopy and X-ray tomography, and hypotheses based upon the observed relationships were formulated to explain the behaviour.

- The experimental and analytical techniques adopted in this project were designed to be entirely novel in the field of nuclear graphite research, or to significantly improve existing techniques. The resulting conclusions have increased our understanding of the response to stress of graphite.

- The results from two-dimensional studies and three-dimensional studies were compared to analyse the suitability of two-dimensional analyses of three-dimensional behaviour.

- X-ray diffraction studies have yielded additional insight into how stresses affect the crystal structure of graphite. However, due to the lack of suitable in-situ deformation stages compatible with the diffractometer, the study was limited by only being able to consider the effects of prestresses.

- Proposals for future research into the response of stresses in graphite have been made.
References


Appendix: Publication of Research

A number of publications have arisen from the work carried out during the completion of this research project. The details of these publications are discussed below:


  This peer-reviewed paper discusses the preliminary confocal laser microscopy experiments that were developed into the experiments discussed in Chapter 4.


  This peer-reviewed paper details the results of investigations into stress-induced variation of pore properties using confocal laser microscopy, as discussed in Chapter 4.


  This peer-reviewed paper discusses some of the observations of stress induced pore deformation observed using X-ray tomography, as discussed in Chapter 5.


  This short paper discusses some of the observations of stress induced pore deformation observed using X-ray tomography, as discussed in Chapter 5.