Structural Features in Heat Transfer Modeling of PEM Fuel Cell Materials

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Department of Mechanical and Industrial Engineering
University of Toronto

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**Abstract**

In this thesis, the impact of incorporating high resolution structural features into the thermal modeling of the polymer electrolyte membrane (PEM) fuel cell gas diffusion layer (GDL) and microporous layer (MPL) is studied. Atomic force microscopy (AFM) has been used to image the surfaces of untreated Toray GDL fibres, and the nano-sized particles within Sigracet MPL. The validity of the GDL smooth fibre assumption commonly employed in literature is studied using a thermal resistance network approach. The MPL, which has been found to show structural variability between manufacturers, was also analyzed using AFM to obtain distributions for the particle size and filling radius. The equivalent thermal resistance between MPL particles was computed using the Gauss-Seidel iterative method, and was found to be sensitive to the particle separation distance and filling radius. Finally, unit-cell analysis is presented as a methodology for incorporating MPL nano-features into modeling of the MPL bulk regions.
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# Table of Contents

Acknowledgements iii  
Table of Contents v  
List of Tables x  
List of Figures xii  
Abbreviations & Nomenclature xvii  

Chapter 1: Introduction 1  
1.1 Preamble 1  
1.2 Motivation and Objective 2  
1.3 Contributions 3  
1.3.1 Journal Manuscripts 3  
1.3.2 Conference Papers (Accompanied by Oral Presentations) 3  
1.4 Organization of Thesis 4  

Chapter 2: Background and Literature Review 5  
2.1 Introduction 5  
2.2 PEM Fuel Cells 5  
2.2.1 Electrochemical Energy Generation 6  
2.2.2 Thermal Energy and Water Management 7  
2.3 Cathode Material Structure and Function 8  
2.3.1 GDL Structure 8
2.3.2 MPL Structure

2.4 Effective Thermal Conductivity

2.4.1 GDL Effective Thermal Conductivity

2.4.2 MPL Effective Thermal Conductivity

2.5 Tables

2.6 Figures

Chapter 3: GDL Fibre Surface Morphology

3.1 Introduction

3.2 Motivation and Objective

3.3 Characterization of GDL Fibre Surfaces

3.4 Methodology

3.4.1 Determination of Fibre Contact Force Range

3.4.2 Surface Fitting of GDL Fibre Data

3.4.3 Determination of Micro-Contact Order

3.5 Contact Mechanics

3.5.1 Micro-Contact Shape

3.5.2 Step-Wise Compression

3.6 Thermal Analysis

3.7 Rough Fibre Contact Area

3.7.1 Micro-Contact Area

3.7.2 Total Contact Area

3.7.3 Curve-Fitting of Total Contact Area Data
3.8 Rough Fibre Thermal Contact Resistance

3.8.1 Thermal Contact Resistance Range

3.8.2 Critical Regions in GDL with respect to Thermal Contact Resistance

3.8.3 Curve-Fitting of Thermal Contact Resistance Data

3.9 Conclusions

3.10 Tables

3.11 Figures

Chapter 4: Characterization of the MPL

4.1 Introduction

4.2 Motivation and Objective

4.3 Characterization of MPL Materials

4.4 Thermal Model

4.4.1 Thermal Model Description

4.4.2 Thermal Model Assumptions

4.5 Thermal Analysis of MPL Particle Contact Types

4.5.1 Effect of Varying Overlapping Distance on Equivalent Thermal Resistance

4.5.2 Effect of Varying Filling Radius on Equivalent Thermal Resistance

4.5.3 Effect of Varying Separation Distance on Equivalent Thermal Resistance

4.5.4 Effect of Varying Particle Diameter Ratio on Equivalent Thermal Resistance

4.6 Conclusions

4.7 Tables
Chapter 5: Unit-Cell Analysis

5.1 Introduction

5.2 Motivation and Objective

5.3 Unit-Cell Reconstruction of MPL Particles

5.3.1 Voxel Resolution Selection Based On Unit-Cell Reconstruction Accuracy

5.3.2 Voxel Resolution Selection Based On Effective Thermal Conductivity Measurement

5.3.3 Irregular Unit-Cells

5.4 Comparison of MPL Particle Features on Unit-Cell Effective Thermal Conductivity

5.4.1 Filled Contact Algorithm

5.4.2 SGL-10BB and SGL-10BC Regular Unit-Cells

5.4.3 SGL-10BB and SGL-10BC Irregular Unit-Cells

5.4.3.1 Irregular Unit-Cell Nomenclature

5.4.3.2 Irregular Unit-Cell Effective Thermal Conductivity

5.5 Validation of the Thermal Model presented in Section 4.4

5.6 Conclusions

5.7 Tables

5.8 Figures

Chapter 6: Conclusions
Chapter 7: Future Work

7.1 GDL Fibre Surface Morphology

7.2 MPL Particle Analysis

7.3 Unit-Cell Analysis

References
List of Tables

Table 2-1. Summary of reported effective thermal conductivity values for GDL, MPL, and GDL+MPL substrates.  

Table 3-1. AFM image surface feature data.  

Table 3-2. Properties of the GDL Carbon Fibres  

Table 3-3. Coefficients matrix for empirical mean total contact area (µm²) and total contact area standard deviation formulae.  

Table 3-4. Coefficients matrix for empirically determined mean thermal contact resistance (K(mW)⁻¹) and thermal contact resistance standard deviation.  

Table 4-1. Statistical information based on the gamma probability distribution regarding MPL particle contacts and particle connections  

Table 5-1. Impact of voxel resolution on accuracy of BCC and FCC reconstruction  

Table 5-2. Voxel resolution for various unit-cell reconstructions  

Table 5-3. Effective thermal conductivity of various unit-cell configurations with air at 80°C as the fluid-phase  

Table 5-4. Effective thermal conductivity of various unit-cell configurations with liquid water as the fluid-phase
Table 5-5. Effective thermal conductivity (Wm$^{-1}$K$^{-1}$) of unsaturated SGL-10BB irregular BCC structures, with a separation distance of 0 nm in $x$-, $y$-, and $z$-directions.

Table 5-6. Effective thermal conductivity (Wm$^{-1}$K$^{-1}$) of unsaturated SGL-10BB irregular FCC structures, with a separation distance of 0 nm in $x$-, $y$-, and $z$-directions.
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Schematic of PEM fuel cell operation.</td>
<td>16</td>
</tr>
<tr>
<td>2-2</td>
<td>SEM Image of Toray GDL.</td>
<td>17</td>
</tr>
<tr>
<td>2-3</td>
<td>Backscatter electron microscopy image comparing GDL fibre size, MPL crack width, and MPL pore size.</td>
<td>18</td>
</tr>
<tr>
<td>2-4</td>
<td>AFM images of SGL-10BC MPL with frame size of 10 μm; Figure 2-4a) 3-dimensional view, Figure 2-4b) Topological view.</td>
<td>19</td>
</tr>
<tr>
<td>2-5</td>
<td>SEM images of SGL-10BC MPL. Figure 2-5a) 100x magnification with scale bar length of 100 μm. Figure 2-5b) 2000x magnification on crack wall. Figure 2-5c) 2000x magnification on crack corner.</td>
<td>20</td>
</tr>
<tr>
<td>3-1</td>
<td>AFM images used in rough contact analysis featuring cylindrical asperities (image b and image f, respectively), protruding irregularities (image a and image c), localized flat-zones (image e), and sharp peaks (image d).</td>
<td>45</td>
</tr>
<tr>
<td>3-2</td>
<td>3D mapping of fibre surface data obtained using AFM for image f.</td>
<td>46</td>
</tr>
<tr>
<td>3-3</td>
<td>Height deviation in the circumferential (a), and longitudinal (b) directions for AFM image a.</td>
<td>47</td>
</tr>
<tr>
<td>3-4</td>
<td>Algorithm used to determine thermal contact resistance and contact area for rough contacting fibres.</td>
<td>48</td>
</tr>
<tr>
<td>3-5</td>
<td>Average Cross-Sections with and without curve fits for AFM images a, c, and f.</td>
<td>49</td>
</tr>
</tbody>
</table>
Figure 3-6. Comparison of micro-contact shapes for two asperities of radii of curvature equal to 100 nm in contact with various contact force, and angle of orientation equal to (a) 45° and (b) 90°.

Figure 3-7. Qualitative representation of heat transfer between rough fibres.

Figure 3-8. Micro-contact area versus contact force for two AFM image type profiles in contact, for an angle of orientation of (a) 30°, (b) 45°, and (c) 90°.

Figure 3-9. Total Contact Area versus Contact Force for Rough and Smooth Cases

Figure 3-10. Total contact area versus contact force for rough and smooth cases for an angle of orientation of 45° (a), and total contact area versus angle of orientation for rough and smooth cases for a contact force of 0.01 N (b).

Figure 3-11. Average total contact area contour plot versus angle of orientation and fibre contact force.

Figure 3-12. Effective thermal contact resistance versus contact force for rough and smooth cases for an angle of orientation of 45° (a), and effective thermal contact resistance versus angle of orientation for rough and smooth cases for a contact force of 0.01 N (b).

Figure 3-13. Effective Thermal Contact Resistance versus Angle of Orientation and Fibre Contact Force

Figure 4-1. SEM image of SGL-10BC showing variance in particle sizes

Figure 4-2 AFM images of SGL-10BB MPL with frame size of 1x1 μm²; Figure 4-2a) 3-dimensional view, Figure 4-2b) Topological view.
Figure 4-3: Comparison of raw AFM data (SGL-10BB) and smoothed data using a span of 30%.

Figure 4-4. SGL-10BB particles (red) and particle connections (blue) circle fitted to the smoothened AFM image height data (black).

Figure 4-5. Particle size distribution for SGL-10BB (a), and SGL-10BC (b).

Figure 4-6. Filling radius distribution for SGL-10BB (a), and SGL-10BC (b).

Figure 4-7. Combined data for SGL-10BB and SGL-10BC; particle size (a) and filling radius (b).

Figure 4-8. Schematic of MPL particle structure (a) boundary conditions and (b) cubic element.

Figure 4-9. Schematic of MPL particle contact types; (a) various overlapping distance with no filling radius, (b) various filling radius with no overlapping or separation distance, and (c) various separation distance with constant filling radius.

Figure 4-10. Schematic (a) and 3D representation (b) of particles with varying diameter in contact. Figure 4-15b shows examples for two Dia1/Dia2: 0.4 and 1.6.

Figure 4-11. Equivalent thermal resistance between MPL particle contacts versus overlapping distance.

Figure 4-12. Comparison of equivalent thermal resistance with air and water as the surrounding fluid, versus overlapping distance.
Figure 4-13. Equivalent thermal resistance between MPL particle contacts versus filling radius.

Figure 4-14. Comparison of equivalent thermal resistance with air and water as the surrounding fluid, versus filling radius.

Figure 4-15. Equivalent thermal resistance between MPL particle contacts versus separation distance.

Figure 4-16. Comparison of equivalent thermal resistance with air and water as the surrounding fluid as a function of particle separation distance.

Figure 4-17. Equivalent thermal resistance between MPL particle contacts versus particle diameter ratio (Dia₁/Dia₂)

Figure 4-18. Particle diameter ratio distribution generated using SGL-10BB and SGL-10BC particle size data (figure 4-5)

Figure 5-1. Schematic of an MPL cross-section, approximately 1 µm by 1 µm, showing the use of unit-cells for population low-resolution MPL reconstructions in 2D; (a) schematic of an MPL cross-section, (b) schematic of a unit-cell populated cross section, and (c) both images overlaid.

Figure 5-2. BCC and FCC reconstructions using various number of voxels

Figure 5-3. Comparison of voxel count in unit-cell reconstruction with analytical results for kₚ/kₘ = 1000, for (a) BCC and (b) FCC structures.

Figure 5-4. Irregular BCC Lattice Structures

Figure 5-5. Irregular FCC Lattice Structures
Figure 5-6. Various SGL-10BB unit-cell configurations, (a) BCC with $d_s = 10.1$ nm, (b) BCC with $d_s = 0$ nm, (c) FCC with $d_s = 10.1$ nm, and (d) FCC with $d_s = 0$ nm.

Figure 5-7. Naming system and co-ordinate axis used to define directional effective thermal conductivities of irregular BCC (a) and FCC (b) unit-cells.

Figure 5-8. Comparison of numerical results with analytical data, for various $k_{solid}/k_{matrix}$, (a) BCC and (b) FCC.

Figure 5-9. Analytical and numerical results for $k_{solid}/k_{matrix} = 100$ (non-infinite), (a) BCC and (b) FCC.
Abbreviations & Nomenclature

PEM Fuel Cell Components:
CL Cataly...
**Chapter 3 Variables:**

- $r_{asperity}$: Asperity Radius
- $P_{GDL}$: Bulk Pressure
- $F_c$: Contact Force
- $TCR$: Effective Thermal Contact Resistance
- $TCR_{avg}$: Effective Thermal Contact Resistance Average
- $TCR_{std}$: Effective Thermal Contact Resistance Standard Deviation
- $k_{fibre}$: Fibre Thermal Conductivity
- $l_{GDL}$: Length of Gas Diffusion Layer
- $r_{eq}$: Micro-Contact Radius
- $A_{mc}$: Micro-Contact Area
- $C_{layer}$: Number of Contact Points Between Layers in GDL
- $\theta$: Orientation Angle
- $T_{sink}$: Temperature Sink
- $T_{source}$: Temperature Source
- $R_{co}$: Thermal Constriction Resistance
- $R_{sp}$: Thermal Spreading Resistance
- $A_{total}$: Total Contact Area
- $A_{total,avg}$: Total Contact Area Mean
- $A_{total,std}$: Total Contact Area Standard Deviation
- $w_{GDL}$: Width of Gas Diffusion Layer
### Chapter 4 and 5 Variables:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{Q}_g$</td>
<td>Conductive Heat Transfer Between Elements in Direction of Initial Temperature Gradient</td>
</tr>
<tr>
<td>$k_{\text{eff, voxel}_i}$</td>
<td>Effective Thermal Conductivity Between Element $i$ and Neighbouring Element</td>
</tr>
<tr>
<td>$k_{\text{eff}}$</td>
<td>Effective Thermal Conductivity</td>
</tr>
<tr>
<td>$k_{\text{matrix}}$</td>
<td>Effective Thermal Conductivity of Fluid-Phase</td>
</tr>
<tr>
<td>$k_{\text{solid}}$</td>
<td>Effective Thermal Conductivity of Solid-Phase</td>
</tr>
<tr>
<td>$R$</td>
<td>Equivalent Thermal Resistance of Structure</td>
</tr>
<tr>
<td>$\dot{Q}_l$</td>
<td>Heat Transfer Between Element Under Consideration and Neighbouring Element</td>
</tr>
<tr>
<td>$\text{Dia}_1/\text{Dia}_2$</td>
<td>Particle Diameter Ratio</td>
</tr>
<tr>
<td>$d_s$</td>
<td>Separation Distance</td>
</tr>
<tr>
<td>$\text{svf}$</td>
<td>Solid-Volume Fraction</td>
</tr>
<tr>
<td>$T_{\text{top}}$</td>
<td>Temperature Boundary Condition (top)</td>
</tr>
<tr>
<td>$T_{\text{bottom}}$</td>
<td>Temperature Boundary Condition (bottom)</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Temperature of Element $i$</td>
</tr>
<tr>
<td>$T_{\text{element}}$</td>
<td>Temperature of Neighbouring Element</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Thermal Conductivity of Carbon</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Thermal Conductivity of Element $i$</td>
</tr>
<tr>
<td>$k_{\text{element}}$</td>
<td>Thermal Conductivity of Neighbouring Element</td>
</tr>
<tr>
<td>$k_{\text{PTFE}}$</td>
<td>Thermal Conductivity of Polytetrafluoroethylene</td>
</tr>
<tr>
<td>$\dot{Q}_{\text{total}}$</td>
<td>Total Heat Transfer at Structure Boundary</td>
</tr>
<tr>
<td>$A_{\text{unit-cell}}$</td>
<td>Unit-Cell Area</td>
</tr>
<tr>
<td>$L_{\text{unit-cell}}$</td>
<td>Unit-Cell Length [nm]</td>
</tr>
<tr>
<td>$a$</td>
<td>Unit-Cell Length [voxels]</td>
</tr>
<tr>
<td>$A_{\text{voxel}}$</td>
<td>Voxel Area</td>
</tr>
<tr>
<td>$d_{\text{voxel}}$</td>
<td>Voxel Width</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Preamble

Polymer electrolyte membrane (PEM) fuel cells are electrochemical energy conversion devices, and have been a main focus of study in the area of clean energy systems in the past decade. PEM fuel cells generate power electrochemically, utilizing hydrogen gas and oxygen from air, forming only water and heat as by-products. Production of hydrogen gas via electrolysis or by other alternatives is becoming more economically and ecologically efficient, with the advancement of renewable energy systems based on solar, wind, hydro, and geothermal power generation.

With growing demand for efficient clean energy systems, PEM fuel cells offer promising advantages over current technologies, such as the internal combustion engine, increasing their potential as a viable alternative in energy conversion. For example, the PEM fuel cell and internal combustion engine energy generation cycles were compared from a thermodynamic, economic, and ecological perspective by Braga et al. [1]. In this study, it was quantitatively determined that PEM fuel cells are more exergetically efficient (producing higher quality of energy) than internal combustion engines, with exergetic efficiencies of PEM fuel cells being approximately 40%, compared to 22% exergetic efficiency for internal combustion engines [1]. PEM fuel cells also produce less greenhouse gas emissions during operation, having ecological efficiencies of 96% compared to 51% for internal combustion engines, based on the emission of carbon dioxide [1]. Automobile companies such as Ford, General Motors, and Nissan are committed to advancing their fleet of fuel cell based cars, with the intention of having them on the market by 2015 [2]. However, before PEM fuel cells can compete with existing technologies in terms of cost, durability, and reliability [1], further advancements in issues regarding thermal
energy and water management within the cathode of the cell must be incorporated into future cell designs.

1.2 Motivation and Objective

The main objective of this thesis is to investigate the impact of high-resolution features in PEM fuel cell cathode materials on their effective thermal conductivity. In particular, two cathode materials are studied at the nano-scale: the gas diffusion layer (GDL) and microporous layer (MPL). By understanding the impact of incorporating these features on heat transfer modeling, more accurate predictions of effective thermal conductivity can be obtained. Using the results of this study, thermal gradients within the cell, which affect the overall cell performance, can be more accurately computed. The results of this study can also inform GDL and MPL manufacturers on limiting features in their designs, helping improve their product by optimizing material tolerances.

The impact of incorporating fibre roughness into analytically calculated fibre-fibre thermal contact resistance is analyzed to test the validity of the smooth-fibre assumption commonly employed in literature. Secondly, the MPL particle connections and particle sizes are studied to investigate the variability among material types, and their impact on the numerically calculated effective thermal conductivity, computed using the Gauss-Seidel iterative method. Finally, a methodology for incorporating the studied nano-structures found within the MPL, based on unit-cell analysis, is presented.
1.3 Contributions

The results of this work have led to the following contributions:

1.3.1 Journal Manuscripts


1.3.2 Conference Papers (Accompanied by Oral Presentations)


1.4 Organization of Thesis

This thesis is organized into 7 chapters in total. In this chapter, a brief description regarding the PEM fuel technology and the thesis motivation/contributions was provided. In chapter 2, details regarding the processes required for electrochemical energy generation are described. The role of thermal energy management and water management in the GDL and MPL, and the impact of GDL and MPL structures on cell performance are also discussed. A detailed review of the
effective thermal conductivity values referenced in literature for the GDL and MPL is also presented in chapter 2. In chapter 3, the impact of fibre surface morphology on the validity of the smooth fibre assumption is studied by calculating the thermal contact resistance between rough fibres. The effect of the fibre circumferential roughness, fibre orientation angle, and fibre contact force on the contact area and thermal contact resistance is explored, with results presented in the form of empirical relations to be used in future studies. In chapter 4, the MPL is analyzed to obtain the particle diameter and particle connection filling radius distributions to investigate the variability of the MPL nano-structures among different material types. The impact of incorporating nano-resolution in the reconstruction of the MPL particles and particle connections is explored, highlighting the effect of altering the nature of contact between particles on the numerically calculated equivalent thermal resistance. In chapter 5, unit-cell analysis is presented as a technique for modeling the MPL nano-features studied in chapter 4, in a macro-model of the MPL. Finally, in chapters 6 and 7, the conclusions to the thesis and highlighted future works are presented respectively.
Chapter 2: Background and Literature Review

2.1 Introduction

In this chapter, the fundamentals of PEM fuel cell operation and the impact of effective heat transfer within the cathode on cell performance are explored. The structures of two critical components of the PEM fuel cell, the GDL and MPL, are described and compared. Also, the existing literature focused on effective thermal conductivity measurement and heat transfer mechanisms within the PEM fuel cell are discussed and summarized.

2.2 PEM Fuel Cells

PEM fuel cells are electrochemical energy conversion devices that have the potential to generate electricity with zero local greenhouse gas emissions, when fed hydrogen gas and oxygen from air. Aside from being a clean energy system with only heat and water as by-products (when hydrogen is used as the fuel), PEM fuel cells offer other promising advantages. For example, PEM fuel cells maintain high efficiency during operation (50%-60% conversion efficiency) [3], supply a high power to volume ratio (0.7 W/cm$^2$) [3], operate with little to no noise, and are able to quickly reach steady state conditions [4] due to their relatively low operating temperature of 80°C [5-7]. In spite of these advantages, PEM fuel cells have issues regarding their:

- *cost* [8], primarily due to the manufacturing of the bipolar plates and use of platinum as a catalyst to improve reaction efficiency,
- *durability* [9], as long-term use causes decreases in mechanical stability of cell components via crack propagation and component delamination [10], and
• reliability [8], as maintaining steady state conditions is sometimes difficult due to their multi-phase nature.

These limitations can be minimized by optimally designing cell components, and by designing cathode materials for enhanced thermal energy and water management. Improvements to the PEM fuel cell design must take place before the technology can broaden its range of viable applications, increasing its profit margins within the booming industry of renewable energy systems [1].

2.2.1 Electrochemical Energy Generation

The PEM fuel cell allows for continuous electrical energy conversion as long as hydrogen, $H_2$, is supplied to the anode, oxygen, $O_2$, is supplied to the cathode, and operational environmental conditions are maintained. When hydrogen is supplied to the anode of the PEM fuel cell, the hydrogen molecule is catalytically broken down into protons, $H^+$, that travel through the polymer electrolyte membrane, and electrons, $e^-$, that travel through an external circuit in the form of electricity. When the protons and electrons meet with the oxygen molecules at the cathode catalyst layer (CL), water is formed exothermically. The cathode half-reaction involved in the formation of water is shown in equation 2.1. A schematic of the PEM fuel cell operation principles is shown in figure 2-1. A detailed study regarding the amount of heat released from the cathode half-reaction involved in water formation can be found in [11], conducted by Ramousse et. al.

\[
2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O + \text{heat}
\]
2.2.2 Thermal Energy and Water Management

The performance of PEM fuel cells is dependent on the effective thermal energy management and water management within the MPL and GDL. However, thermal gradients in the diffusion media (MPL and GDL) and the saturation of liquid water are both coupled, making control of these parameters through the design of the MPL and GDL structures quite difficult. For example, while both heat and water are formed exothermically at the interface between the MPL and CL (MPL|CL), heat is also produced from joule heating (ohmic resistance to electron flow in the solid-space of the diffusion media) and water phase change [6,12]. Heat is introduced with the inlet gases, which facilitates higher humidity in the cathode of the PEM fuel cell, helping hydrate the polymer electrolyte membrane. Hydrating the membrane assists in minimizing fluctuations from low to high current densities [13], as the membrane’s structural properties and ionic conductivity (conduction of $H^+$) are very sensitive to the membrane’s hydration levels [14,15]. Although water is required to hydrate the membrane, too much water in the MPL causes mass transport losses (attributed to the increased tortuosity of the path reactant gases must take to the reaction site) [16-19], causing fluctuations in current density. Also, during operation, delamination in the MPL|CL may occur due to the fluctuation of water levels caused by temperature changes [4]. Delamination between the MPL and CL can lead to an increase in ohmic resistances at the MPL|CL which affects water saturation levels and the cell’s performance [4,20]. Finally, heat sinks and sources are introduced whenever water evaporates or condenses, respectively, which is dependent on the local saturation pressure and temperature, further complicating the cathode temperature gradient and pathway for thermal conduction [15]. Nonetheless, there is a delicate balance between the water saturation (liquid and vapour) and temperature levels in the PEM fuel cell which must be controlled in order to optimize
performance. Therefore, understanding how material structures affect heat transfer, water permeability, and reactant gas/water vapour diffusion is critical for advancing the design of cell components.

2.3 Cathode Material Structure and Function

The GDL and MPL are both porous materials used as domains for which the mechanical and chemical processes required for energy generation can take place. The pore sizes in the GDL are approximately two orders of magnitude larger than the pore sizes in the MPL. With the exception of cracks in the MPL [21], the pore sizes in the MPL are on the order of nanometres [22] while pore sizes in the GDL are on the order of micrometres [23,24]. The main functions of the two materials are to assist in water management and thermal energy management through the design of the solid-space and pore-space. In particular, the GDL and MPL designs provide:

- a pathway for thermal and electrical conduction in the solid-space,
- a path for inlet gas diffusion in the pore-space,
- a pathway for liquid water permeation through pore-space, and
- structural integrity to the design of the PEM fuel cell.

2.3.1 GDL Structure

The GDL is composed of carbon fibres, with mean diameter of 7.32 µm [5,20,25], which are often bound together using a polymeric binding agent to improve the structures stability and effective thermal conductivity (by increasing the contact area between fibres). The GDL fibres are coated with polytetrafluoroethylene (PTFE) to increase the structure’s hydrophobicity. The GDL is located between the bipolar plates and CL. GDLs come in three different structures; paper, cloth, and felt, with paper being most popular of the three structures due to its ease of
manufacturing and its ability to be modeled easily (consisting of stacked, relatively straight fibres), helping its design evolve more quickly [7,26,27]. Carbon is used in the GDL structure due to its exceptional mechanical properties, including a high stiffness to density ratio, and high thermal/electrical conductivity. The thickness of the GDL is approximately 200 µm. Figure 2-2 includes a scanning electron microscopy image of a commercially available Toray GDL, illustrating the random nature of the GDL structure and size-scale of the fibres.

2.3.2 MPL Structure

The MPL is a nano-porous material, composed of agglomerations of carbon particles which range in diameter (on the order of nanometres), bound together with PTFE filling, with the features of the MPL being two orders of magnitude smaller than that of the GDL. Figure 2-3 includes a backscatter electron microscopy image showing the relative size of the MPL solid-space, GDL fibre, and MPL cracks. The MPL is usually coated onto one side of the GDL near the CL, acting as either a:

- fully-immersed coating, where the MPL exists within the pore-space of the GDL,
- partially-immersed coating, where part of the MPL is within the GDL pore-space and the other part is its own layer, or
- standalone structure [6].

The MPL is a relatively new material structure used in PEM fuel cell operation with growing interest as studies have shown that the incorporation of an MPL improves cell performance (current density and voltage potential) [28]. Though the direct impact of the MPL is somewhat unknown, it has been postulated that the MPL improves cell performance by:
• minimizing ohmic resistances between the CL due to the surface pores in the MPL being smaller than that of the GDL [29],
• improving water management due to the its:
  o highly hydrophobic nature, permeating water through the MPL cracks and large pores [30], and
  o larger temperature gradient, affecting the humidity gradient in the through-plane direction of the MPL, helping diffuse water vapour away from the reaction site [31], and by
• improving structural integrity of the cathode by protecting the membrane from overhanging GDL fibres which may puncture the membrane, causing reactant crossover.

Figure 2-4 includes an AFM image of the surface of SGL-10BC (a commonly used, commercially available MPL material). As can be seen, the surface of the MPL is quite rough, comprising of many particles. The MPL usually contains surface cracks [23], which do not necessarily traverse through the entire thickness of the MPL. It is hypothesized that the cracks in the MPL structure arise due to thermal shock in the cooling process following the sintering process used to bind the material together, and are located directly above surface fibres in the GDL [32]. The cracks have the unintended function of acting as the main pathway for water permeation from the MPL|CL [30], freeing up area for reactant gases to become involved in electrochemical energy generation. Figure 2-5 shows an SEM image of the SGL-10BC’s surface, zoomed in on the surface cracks. The cracks shown in figure 2-5a help permeate liquid water away from the CL [32], though it is difficult to control their size and location, as their formation is sporadic. As can be seen in figure 2-5b (a magnified image of one of the cracks) these cracks do not necessarily penetrate through the entire thickness of the MPL, nor have constant shape,
though that is how they are commonly modelled [29,33]. Also, the walls of the cracks are rough, which would affect the advancing contact angle of liquid water traversing through the thickness of the MPL away from the MPL|CL. Figure 2-5c is a magnified image of one of the crack corners. As can be seen, there also exists over-hanging MPL particle agglomerations in the void regions of the structure, which make up the MPL solid-space.

Though the MPL assists in water management in the PEM fuel cell, due to the high PTFE content, incorporation of a MPL tends to lower the overall effective thermal conductivity of the diffusion media [8]. Therefore, there is a growing interest in optimizing the design of the MPL structure via computational modeling [21,34]. However, due to the structures variability among manufacturer and material type, validation of MPL models is difficult [22].

2.4 Effective Thermal Conductivity

In order to analyze how well various GDLs and MPLs conduct heat, their effective thermal conductivity is measured. Measurements have been obtained experimentally and numerically through the use of modeling of the diffusion media structures. It has been found that the GDL fibrous substrate effective thermal conductivity varies between the through-plane and in-plane directions [35] while the MPL displays isotropic effective thermal conductivity and diffusion properties [22]. Due to both the variability in the MPL structure [22] and difficulties in distinguishing between the GDL and partially-immersed MPL structures, the reported effective thermal conductivities range drastically [22]. Table 2-1 includes a summary of the findings in literature for the effective thermal conductivities of the GDL, MPL, and GDL+MPL substrates.
2.4.1 GDL Effective Thermal Conductivity

Several numerical approaches, including analytical modeling [7,9,26,36], use of GeoDict and Fluent [37], and lattice Boltzmann methods (LBM) [5,25,38,39], have been used to characterize the GDL effective thermal conductivity in the through-plane and in-plane directions with respect to multiple parameters controlling the structure of the GDL. It has been found that the GDL effective thermal conductivity in the through-plane direction ranges from approximately 0.5 – 2 Wm\(^{-1}\)K\(^{-1}\), having a positive correlation with:

- GDL compression [7,9,36],
- PTFE content [36], and
- water saturation [25].

The GDL through-plane effective thermal conductivity has a negative correlation with:

- perpendicularly of fibres [9], related to the fibre contact area,
- mean temperature of the solid-space (shown both numerically via Fluent [37] and experimentally [40]), controlling the thermal properties of carbon, and
- porosity, determined using numerical modeling [5,9,37] and experiment [41,42].

The GDL effective thermal conductivity in the in-plane direction is approximately 5-10 times higher than that of the through-plane direction [5,26,37]. This result is expected since the fibres are orientated with central axes approximately orthogonal to the through-plane normal direction. The in-plane effective thermal conductivity has been found to increase with water saturation [25], decrease with porosity [5,37], and remain constant with PTFE content (unlike for the
through-plane direction) [26]. Nonetheless, the GDL has been modeled quite extensively, and the findings in literature have been used to further develop the structures of these materials.

2.4.2 MPL Effective Thermal Conductivity

The effective thermal conductivity of the MPL as a standalone material (based on FIB-SEM reconstruction) has been documented to be approximately isotropic, ranging from 0.13 Wm⁻¹K⁻¹ to 0.29 Wm⁻¹K⁻¹ in its uncompressed state [22]. The MPL effective thermal conductivity range presented in [22] varied based on PTFE content used in the MPL reconstruction, which directly impacted the thermal resistance between MPL particles. The effect of pressure applied to the GDL+MPL substrate has been studied in [8,43], where it has been found that the effective thermal conductivity of the GDL+MPL increases with compression, ranging from approximately 0.3 – 0.6 Wm⁻¹K⁻¹ when compressed from 200 kPa to 1400 kPa [8,43]. Burheim et. al [6] experimentally studied in-house MPL structures, and found no significant change in the MPL effective thermal conductivity with PTFE content. The effect of compression on the MPL as a standalone material has been investigated, where experimental measurements by Burheim et. al [6] found that the MPL effective thermal conductivity increased from approximately 0.075 Wm⁻¹K⁻¹ to 0.12 Wm⁻¹K⁻¹ when the applied pressure increased from 460 kPa to 1380 kPa; close to the lower bound presented in [22]. However, Unsworth et. al [8] reported that due to the structural stability of the MPL, the effective thermal conductivity does not change with compression, remaining relatively constant at approximately 0.3 Wm⁻¹K⁻¹ [8]; close to the upper bound presented in [22]. As can be seen, there is a discrepancy in reported effective thermal conductivity values, which makes validation of numerical models of the MPL difficult. For example, Nanjundappa et. al [22] found that throughout the literature, the reported
MPL effective thermal conductivities range from approximately 0.04 Wm$^{-1}$K$^{-1}$ to 4 Wm$^{-1}$K$^{-1}$, which may be a function of:

- structure variability,
- uncertainty of experimental measurement,
- difficulty in characterizing the penetration depth of immersed MPLs into GDLs, and
- underestimation of the GDL-MPL interfacial thermal contact resistance.

Due to the wide range of experimentally determined effective thermal conductivity values for the MPL substrate, numerical modeling of the MPL structure is arising as a novel approach to characterizing the effective transport properties. Becker et. al [21,37] studied the MPL effective thermal conductivity dependence on the MPL structure, and found that the MPL effective thermal conductivity increases with decreasing mean pore size. Also, Becker found that increasing the penetration depth of the MPL into the GDL also improves the effective thermal conductivity of the GDL+MPL substrate [37], but reduces the effective diffusion coefficient. This result is in agreement with the experimental findings of Burheim et. al [6], who found that having the MPL as a fully-immersed material resulted in an average increase in solid-space temperature of 2°C due to the increased effective thermal conductivity. Nonetheless, more work needs to be done on both experimental and numerical determination of the MPL effective thermal conductivity; which is expected since the introduction of the MPL as a PEM fuel cell component is still relatively novel.
### 2.5 Tables

<table>
<thead>
<tr>
<th>Material</th>
<th>Effective Thermal Conductivity</th>
<th>Positive Correlation</th>
<th>Negative Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDL (through-plane)</td>
<td>• 0.5 – 2 Wm⁻¹K⁻¹</td>
<td>• GDL compression [7,9,36]</td>
<td>• Perpendicularity of fibres [9]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• PTFE content [36]</td>
<td>• Mean temperature of solid-space [37,40]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Water saturation [25]</td>
<td>• Porosity [5,9,37]</td>
</tr>
<tr>
<td>GDL (in-plane)</td>
<td>• 5 – 15 Wm⁻¹K⁻¹ [5,26,37]</td>
<td>• Water Saturation [25]</td>
<td>• Porosity [5,37]</td>
</tr>
<tr>
<td>GDL+MPL</td>
<td>• 0.3 – 0.6 Wm⁻¹K⁻¹ [8,43]</td>
<td>• Substrate compression [8,43]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Penetration depth of MPL [6,37]</td>
<td></td>
</tr>
<tr>
<td>MPL (isotropic)</td>
<td>• 0.13 – 0.3 Wm⁻¹K⁻¹ [8,22]</td>
<td>• GDL compression (slight increase reported in [6], no increase reported in [8])</td>
<td>• Mean pore size [21,37]</td>
</tr>
<tr>
<td></td>
<td>• 0.075 – 0.12 Wm⁻¹K⁻¹ [6]</td>
<td></td>
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</tbody>
</table>

Table 2-1. Summary of reported effective thermal conductivity values for GDL, MPL, and GDL+MPL substrates.
2.6 Figures

Figure 2-1. Schematic of PEM fuel cell operation.
Figure 2-2. SEM Image of Toray GDL.
Figure 2-3. Backscatter electron microscopy image comparing GDL fibre size, MPL crack width, and MPL pore size.
Figure 2-4. AFM images of SGL-10BC MPL with frame size of 10 μm;
Figure 2-4a) 3-dimensional view, Figure 2-4b) Topological view.
Figure 2-5. SEM images of SGL-10BC MPL. Figure 2-5a) 100x magnification with scale bar length of 100 μm. Figure 2-5b) 2000x magnification on crack wall. Figure 2-5c) 2000x magnification on crack corner.
Chapter 3: GDL Fibre Surface Morphology

3.1 Introduction

In this chapter, the impact of incorporating fibre surface morphology in the thermal analysis of the PEM fuel cell GDL is investigated. Using atomic force microscopy (AFM), fibre roughness in the circumferential direction is fitted to obtain asperity height information, which is used to test the validity of the smooth fibre assumption. Greenwood’s rough contact model was implemented to obtain the rough fibre contact area, and thermal contact resistance between contacting rough fibres, for various contact force and angles of orientation. The analysis conducted in this chapter provides a tool which can be used to incorporate the surface features of GDL fibres into existing effective thermal conductivity models, representing more realistic GDL structures.

3.2 Motivation and Objective

Numerical modeling has become a popular approach in aiding the design process of novel GDL materials. Numerical modeling can be used to simulate the performance of PEM fuel cells with respect to the multitude of parameters which affect the cell performance [44], which is difficult to do via experimentation. It has been found that the dominant mechanism for thermal energy out of the GDL is conduction through the carbon fibre network [11,39]. Several thermal conductivity models exist for analyzing thermal conduction within the PEM fuel cell. Lattice Boltzmann methods (LBM) have been used for determining the through-plane and in-plane thermal conductivity of the GDL because of their ability to model complicated structures effectively, and have been used to study both saturated [25,39] and unsaturated [35,38] GDLs. Using LBM, it
was found that the effective thermal conductivity of the GDL increases with water saturation, with a more significant impact in the through-plane direction rather than the in-plane direction [25]. Also, models based on analytical equations have been commonly used for characterizing the effect of compression on the effective thermal conductivity of the GDL [7,36], by characterizing the nature of contact between smooth fibres using Hertzian contact mechanics. It was found that the thermal resistance in the GDL is dominated by the fibre-to-fibre contacts, and the through-plane effective thermal conductivity increases linearly with GDL compression [36].

Although the effective thermal conductivity of the GDL has been studied, it was commonly assumed that the surfaces of the carbon fibres are smooth [7,20], or that the reconstruction resolution corresponding to the lattice spacing in LBM simulations was sufficient for modeling heat flow between contacting fibres. However, as the development of a realistic thermal representation of the GDL continues to evolve, the effect of fibre structural features in the GDL are being considered. For example, the effect of fibre waviness in the longitudinal direction has been studied in a recent publication (2014) by Sadeghifar et al. [45], showing a growing interest in the validity of the simplistic nature of the assumptions controlling the representation of fibres; assumed to be smooth and straight. The objective of this study is to investigate the impact of incorporating realistic fibre surface morphology, in particular the circumferential fibre roughness, on effective thermal conductivity measurement in GDLs. Using an analytical approach based on Greenwood’s rough contact model [46], the thermal contact resistances and contact areas between rough fibres housed in the GDL are analyzed and compared with smooth fibre representations to test the validity of the smooth fibre assumption. The results of this study, published in [47], could be incorporated into other existing effective thermal conductivity
models, further advancing effective thermal conductivity measurement to reflect what occurs during PEM fuel cell operation.

3.3 Characterization of GDL Fibre Surfaces

Carbon fibres housed in untreated Toray GDL were analyzed using AFM. A Nanoscope IIIa Multimode (Digital Instruments) atomic force microscope, located at the Canadian Centre for Electron Microscopy at McMaster University, Ontario, was used to image Toray TGP-H-120 carbon fibre paper without polytetrafluoroethylene (PTFE) treatment. Fibres from the top layer of the GDL were imaged to obtain the following surface feature information:

- roughness in the circumferential and longitudinal directions,
- surface area, and
- height deviations caused by protruding asperities or irregularities.

The longitudinal roughness differs from the fibre waviness. The roughness in this context can be viewed as the deviation in the distance between the fibre surface to the central axis of the fibre in the direction considered (circumferential or longitudinal). The waviness however can be viewed as the path which the central axis of the fibre follows, where a straight central axis would correspond to a non-wavy fibre [45].

AFM images from two locations for three fibres within untreated GDL samples are shown in figure 3-1. The six AFM images in figure 3-1 feature large and small asperities (image b and image f, respectively), protruding irregularities (image a and image c), localized flat-zones (image e), and sharp peaks (image d). A scanning frequency of 1.001 hertz with the atomic force microscope in tapping mode was used to obtain the images with dimensions of 3 µm by 3 µm. The image dimensions were determined by the expected size of the contact area shape based on
findings from previous studies assuming smooth fibre contact [7,20]; the contact area does not exceed this boundary for the forces and orientation angles considered. Table 3-1 includes statistical information regarding the surface features for each of the AFM images from figure 3-1, including the root-mean square (RMS) roughness and surface area. Since the rough fibres are nominally cylindrical in shape, with an assumed nominal carbon fibre diameter of 7.32 µm [20], the roughness values in table 3-1 were obtained by plane-fitting the height information to a cylindrical plane [48]. The AFM images display roughness about the cylindrical surface (the nominal shape of the fibre), and therefore the plane-fit represents the height deviation with respect to the nominal diameter, and was not calculated assuming the nominal surface was flat. The plane-fit was performed in the x-direction of the AFM images shown in figure 3-1, as all fibres were oriented with their central axis parallel to the y-direction.

Using the AFM height data, a three-dimensional mapping of the fibre surfaces were obtained using MATLAB. Figure 3-2 shows an example of one of the 3D meshes, for AFM image f in figure 3-1. The image depicted in figure 3-2 includes the surface features of a section of an individual carbon fibre found in the GDL. In the AFM images, the x- and y-axes represent the spatial co-ordinate of the AFM image, while the z-axis represents the height of the surface. There is an appreciable degree of roughness in the x-direction (the circumferential direction of the fibre), as opposed to the y-direction (the longitudinal direction); this was also observed in [49,50]. An example fibre height profile for image a is shown in figure 3-3. Equally spaced slices were taken through the length and width of the AFM images to obtain roughness profiles.

While the waviness of the fibres in the longitudinal direction may have an important effect on the nature of contact between the GDL fibres and flat surfaces, such as the bipolar plate [45], the
focus of this work is to evaluate the fibre-to-fibre contact within the bulk region of the GDL. The fibre roughness in the circumferential direction was found to be more impactful than the roughness in the longitudinal direction. For example, figures 3-3a and 3-3b show the height profiles of various cross-sections, traversing through the AFM images in the (a) circumferential and (b) longitudinal directions for AFM image a. As can be seen in figure 3-3b, the surface is relatively smooth along the fibre length, showing a single asperity deviation in height. Similar trends were found for the other cases. Throughout the various AFM images, it was found that the largest deviation in height along the longitudinal direction caused by roughness (excluding inclusions on the fibre surface) was approximately 50 nm, which is negligible considering the degree of roughness in the circumferential direction (figure 3-3a). Height profiles for cross-sections at different positions along the length of the fibre are shown in figure 3-3a, and show no significant change in cross-section. The bolded curve represents the nominal diameter of the fibre [20] and was curve-fitted to each of the respective AFM images using a RMS approach. As can be seen, although the cross-section is relatively constant along the 3 µm length of the fibre, the circumferential roughness causes a significant variation from the assumed smooth fibre profile, shown in the deviation of the rough fibre cross-sections compared to the smooth fibre profile (bolded curve).

3.4 Methodology

An analytical approach was used to determine the contact area and thermal contact resistance between rough fibres. Pairs of fibre surface profiles were analyzed for a range of contact forces that would be expected within the GDL of an assembled fuel cell. A range of fibre orientation angles from 15° to 90° was studied. The mechanical and thermal properties used in the study
(Table 3-2) were assumed to be isotropic. Figure 3-4 shows the algorithm used for calculating the contact area and thermal contact resistance of GDLs.

### 3.4.1 Determination of Fibre Contact Force Range

The range of contact forces was determined using the results of a previous study, where Tablecki et al. [20] developed analytical formulations for the number of contact points between adjacent layers of fibres in compressed GDLs. These formulations were derived from micro-computed tomography data [51] yielding porosity distributions for compressed GDLs. Using the porosity distributions, this group numerically constructed GDLs based on the nominal diameter and length of fibres housed in commercial GDLs, while assuming the fibres were preferentially stacked and allowed to overlap within adjacent layers. The number of contacts between fibres in adjacent layers was then determined using the numerically reconstructed GDLs, and presented as a function of orientation angle and average layer interface porosity [20]. The total number of contact points (on average) between layers within the GDL for various GDL thicknesses was then determined [20]. The range of contact forces experienced by the fibres in contact was then found using equation 3.1 [20], where \( F_c \) is the contact force experienced between touching fibres when a GDL section of length \( l_{GDL} \), and width \( w_{GDL} \) is exposed to a through-plane bulk pressure of \( P_{GDL} \). The bulk pressure used to compress the GDL during operation typically ranges between 460 kPa and 1390 kPa [20,52]. Though these are just bulk values, the actual pressure the GDL will experience is dependent on the location of the GDL section (under the ribs or channel of the bipolar plates).

\[
(3.1) \quad F_c = \left( \frac{P_{GDL} l_{GDL} w_{GDL}}{G_{layer}} \right)
\]
Equation 3.1 assumes the contact force is evenly distributed among the number of contacts between the two layers, defined as $C_{layer}$. It was found that the maximum contact force occurs between the layers with largest porosity values. The largest contact force experienced between contacting fibres was calculated to be 0.01 N. Therefore, this value was used as an upper-bound when parameterizing the contact area and thermal contact resistance with the contact force. The contact forces between fibres are difficult to verify due to the complexity of the GDL structure. However it is hypothesized that the low contact force regions in the GDL, such as beneath the bipolar plate channels, is best reflected by forces less than 0.002 N. Therefore, the contact force range from 0 and 0.002 N is critical in the thermal contact resistance analysis presented in this chapter, and is discussed in more detail in section 3.8.1.

3.4.2 Surface Fitting of GDL Fibre Data

The first step in the algorithm shown in figure 3-4 is the input of the fibre contact profiles, which are different than the AFM images shown in figure 3-1. The fibre contact profiles represent analytical mappings of each asperity, comprised of a diameter and position. It was assumed that the cross-section of the fibres could be arithmetically averaged across the 3 µm length of each AFM image, since there was no appreciable degree of roughness in the longitudinal direction. Therefore, the protruding asperities were curve-fitted in each of the average cross-sections with circular curves. The diameters and heights of the circular curves were obtained using a RMS curve fit, as described in [48]. The assumption that the average cross-section could be used along the 3 µm length of AFM images implies that the asperity surfaces are cylindrical. The curve fits for three of the six AFM images from figure 3-1 are shown in figure 3-5.
3.4.3 Determination of Micro-Contact Order

Once two fibre contact profiles have been selected for analysis, the next step is to determine the number of micro-contacts. A micro-contact is formed when an asperity of one fibre comes into contact with an asperity of another fibre. The number of potential micro-contacts is the product of the number of asperities for the two fibre contact profiles considered. The red asperity curve shown for AFM image a is a special case, which will be described in detail in section 3.5.

For this study, the maximum force considered is 0.01 N, which is not large enough for the lowest asperities to come into contact with the tallest ones. Therefore, the next step in the analysis is to determine the order in which the micro-contacts potentially come into contact. For two non-parallel fibres coming into contact with an angle of orientation (θ), the order of contact is solely determined by the height of each individual asperity. In essence, the two asperities with highest peaks will come into contact first. If fibres were to be compressed together further, a second contact would be formed when one of the two initially contacting asperities meets the next tallest asperity, and so on. The distinct order of the contacts can be described as the ranking of the summed heights of all combinations of asperities for the two fibre contact profiles considered.

Once the contact problem has been fully described using the input information of the contact order, the angle of orientation is considered. In this study, an angle of orientation of 90° means the projection of the central axis of the top fibre is orthogonal to the central axis of the bottom fibre. The 0° case consisting of parallel contacting fibres is not considered in this study.
3.5 Contact Mechanics

The method used in this study for analysing the contact between two rough fibres is based on a step-wise compression algorithm evolved from Greenwood’s rough contact model [46]. Since the protruding asperities in this study are fitted with circular curves, the asperities in contact are treated as micro cylinders, rather than spherical tips as in the Greenwood model [46]. Moreover, since there are relatively few asperities within the 3 µm by 3 µm domain, micro-contact analysis is performed individually rather than stochastically via probabilistic functions [33] or by using Fourier transforms [29]. In this study, the well-established Hertzian contact mechanics formulations [53] are used to determine the micro-contact area and fibre normal displacement (penetration displacement), while ensuring the maximum pressure is less than the tensile strength for the carbon fibres [54]. It is assumed that the individual asperities are smooth, continuous, and non-conforming surfaces, which are compressed together while neglecting friction. The Hertzian equations are valid for small strains, which lead to stresses remaining in the elastic region for these surfaces.

3.5.1 Micro-Contact Shape

The Hertzian equations used to model the contact between the micro-cylinders, generated using the GDL fibre asperities, can be found in chapter 4 in the work of Johnson [53]. The analytical approach to fully characterizing the contact between two cylinders forming normal, Hertzian elastic contact is presented and explained in detail. In order to analyze the micro-contact area between two rough GDL fibres, the elastic modulus, Poisson ratio, contact force, radii of curvature of the two asperities, and angle of orientation are needed. The shapes of the micro-contacts are generally elliptical and are dependent on the orientation angle and cylinder diameters, while the area of the micro-contacts is dependent on the contact force. For the special
case of the orientation angle being 90° and cylinders in contact being equal in diameter and mechanical properties, the micro-contact shape is circular. Figure 3-6 shows an overview of the contact shapes for two arbitrary asperities with radii of curvature equal to 100 nm and equal mechanical properties (as would be the case for contacting GDL fibres), for various contact forces and angles of orientation. In figure 3-6, the grey regions represent the regions of the asperities in contact (not the entire fibre), the red dashed line represents the orientation of the major axis of the elliptical contact area, and the green and blue + green regions represent the contact regions for the various contact forces. The dotted black lines represent the central axis of the two contacting cylindrical asperities. It is important to note that figure 3-6 shows an example of a micro-contact. The actual modeled contact area between rough fibres will be comprised of multiple micro-contacts, with varying size and shape.

3.5.2 Step-Wise Compression

The step-wise compression algorithm begins with the two highest asperities forming point contact. At each step, the contact force is increased, and Hertzian analysis is used to determine the contact area and normal displacement at the locations of the micro-contacts. As the contact force continues to increase incrementally, a second micro-contact may form when the fibre normal displacement is sufficiently large. When more than one micro-contact occurs, the increment in contact force is distributed amongst the micro-contacts. At the instance where the second contact is formed, the asperities forming the initial micro-contact have already been compressed a certain amount. Therefore, in order to compensate for the elastic compression imposed up until this point, the increment of the contact force, rather than the total contact force, is split up evenly amongst the micro-contacts in the following iteration [55]. Therefore, it is
assumed that the fibres are vertically compressed into each other (without rotation about the fibre axis), without slippage.

During each step, the contact force is incremented, the algorithm determines which asperity combinations form micro-contacts, and Hertzian analysis is used to calculate the elliptical micro-contact area and normal displacement of the fibres for each micro-contact. The area of each micro-contact is calculated independently, and the effect of neighbouring asperities is assumed to be negligible in this study since the contact forces are small [55]. The contact area was examined to exclude overlapping micro-contact regions with the notion of macro-asperities.

In some cases, since the mean surface is curved rather than smooth, the curve fitted regular asperities (shown in blue in figure 3-5) do not represent the rough fibre surface well. For example, in figure 3-5, image a, the rightmost regular asperity fits the protrusion from the surface well, but not the entire fibre profile. Macro-asperities, such as the curve shown in red in figure 3-5, image a, are used to account for these special cases where it appears that there is an asperity on top of an asperity. The goal of using the notion of macro-asperities is to better approximate the contact area, and is commonly used in models comparing various magnification levels of surfaces [56]. For example, considering AFM image a (figure 3-5) coming into contact with a flat-surface, initially, the rightmost regular asperity (blue) will be used to define the contact between the two surfaces. However, once the normal displacement exceeds (approximately) 100 nm, the surface of the fibre becomes much wider, as the compression of the regular asperity caused the flat surface to come into contact with the macro-asperity region of the fibre. Therefore, in subsequent force increments, the properties of the macro-asperity are used in calculating the increase in contact area and normal displacement [53]. The model automatically utilizes the notion of macro-asperities to account for irregular surface features,
where smaller asperities appear to be on top of larger asperities. It is important to note that the initial compression of the *regular asperity* would cause resistance to further compression once the *macro-asperity* information is used in the contact advancement due to the pressure attributed to the micro-contact. This is accounted for by appending the normal displacement of the *macro-asperity* to the initial compression of the *regular asperity*, and by continuing to calculate the maximum pressure (located at the centroid of the micro-contact area) using the original *regular asperity* curvature.

### 3.6 Thermal Analysis

Once the contact area is determined, the next step is to calculate the effective thermal contact resistance between the contacting rough fibres. The effective thermal contact resistance (*TCR*) is calculated using an equivalent resistance network consisting of the constriction and spreading resistances of each of the individual micro-contacts [57]. In this study, it was assumed that the only heat transfer occurring between the fibres was steady, thermal conduction through the carbon solid space. Thermal conduction along the length of the fibres was not calculated, as it is commonly assumed to be negligible in comparison to the spreading and constriction resistances [7,9,20]. Since untreated fibres (with PTFE) were analyzed, the effect of PTFE agglomeration near the fibre contacts was not considered. Also, the effect of interstitial fluid thermal conductivity on the constriction/spreading resistance was not analyzed, although the thermal conduction would be dominated by the solid pathways through the carbon material, as the carbon thermal conductivity is much greater than that of other species found in the GDL [20]. Heat transfer caused by convection was found to be negligible by Ramousse et al. [58] as the velocity of fluids through the interstitial spaces and surrounding the fibres is miniscule. Radiative heat
transfer is negligible for temperatures below 1000 K [39], which is the case for PEM fuel cells operating at temperatures of approximately 80°C (353 K).

Figure 3-7 depicts a representation of the thermal and mechanical phenomena occurring during fibre contact [59]. The thermal energy is transferred between rough fibres through the micro-contacts. Each of the micro-contacts has their own respective spreading and constriction thermal resistances [46]. The equivalent thermal resistance network used to determine the TCR between two rough fibres with temperatures of $T_{\text{sink}}$ and $T_{\text{source}}$ is obtained by summing the constriction ($R_{co}$) and spreading ($R_{sp}$) resistances in series, then by adding the sums ($R_{co} + R_{sp}$) in parallel [46]. The formulations used to determine the thermal contact resistance for the micro-contacts are provided by Cooper et al. [57]. Here, it is assumed that the thermal domain can be treated as a flux-tube geometry considering the effect of neighbouring asperities [59]. The formulation used is presented in equation 3.2, where asperity radius ($r_{\text{asperity}}$) depends on which asperity is forming the micro-contact, the thermal conductivity of the fibre ($k_{\text{fibre}}$) is 120 Wm$^{-1}$K$^{-1}$, and the equivalent micro-contact radius ($r_{eq}$) is calculated using the micro-contact area ($A_{mc}$): $r_{eq} = \sqrt{A_{mc}/\pi}$, which is determined using the steps outlined in section 3.5.2. Once the micro-contact areas are obtained, the thermal contact resistance per micro-contact can be calculated using equation 3.2, from which the effective thermal contact resistance ($TCR$) can be computed.

$$\text{(3.2) } R_{sp/co} = (1 - \frac{r_{eq}}{r_{\text{asperity}}})^{1.5}/(4k_{\text{fibre}}r_{eq})$$
3.7 Rough Fibre Contact Area

Sections 3.7 and 3.8 includes the results obtained for the analyses for contact area and thermal contact resistance between two rough GDL fibres, respectively. Since the surface morphology can vary between different fibres [49], there is a multitude of contact combinations which can occur. For example, the combinations studied in this analysis could include 256 cases formed by cross-referencing each of the AFM images, and by vertically and/or horizontally rotating fibre contact profiles prior to the analysis. Each case was analyzed for various angles of orientation and contact force.

3.7.1 Micro-Contact Area

Figure 3-8 depicts the micro-contact area versus contact force for the case of two fibre profiles with AFM image a surface information coming into contact for various angles of orientation. In these figures, each of the curves corresponds to the growth of an individual micro-contact area as the contact force is increased. For example, since profiles shown in figure 3-8 both have two asperities, having them come in contact will lead to 4 micro-contacts (four curves). In each of the three sub-figures shown in figure 3-8, some micro-contacts are formed after the initial contact. One point of interest in these figures is the change in slope of the individual contact areas. As can be seen, the rate of change of the micro-contact area with contact force decreases as new contacts are formed. The proportionality of the micro-contact area ($A_{mc}$) with the contact force ($F_c$) in figure 3-8 is $A_{mc} \propto F_c^{2/3}$, which is in line with the results of Hertz, presented by Persson in [56], and also mentioned in [46,60]. Also, the total contact area for this fibre contact combination ($A_{total}$), as shown in figure 3-9, tends to increase linearly with contact force (with values larger than 0.002 N) such that $A_{total} \propto F_c$, which is in agreement with contact models that have the ability to form new contacts [56].
Figure 3-8 also shows the effect of altering the orientation angle on the micro-contact area; the micro-contact area decreases as the angle of orientation approaches 90°, due to there being a smaller projection of the top fibre onto the bottom fibre. When the asperities in contact have equal diameter and mechanical properties (as in the case depicted in figure 3-7c), the micro-contact shape is circular, as shown in figure 3-6. For angles of orientation of 30° and 45°, the micro-contact area shape is elliptical, yielding larger contact areas than the orthogonal case.

3.7.2 Total Contact Area

The total contact area is a summation of the individual micro-contact areas. Figure 3-9 includes total contact area values for the base cases depicted in figure 3-8, and as well as data for two smooth fibres in contact (with no micro-asperities). The total contact area for the rough cases is significantly less than the total contact area for the smooth fibre cases for fibre contact force range and orientation angle range considered.

Figure 3-10a shows the total contact area versus the contact force at a constant angle of orientation of 45° and versus the angle of orientation at a constant contact force of 0.01 N (figure 3-10b). In these images, the dashed line represents the smooth fibre case; fibres with no asperities. The smooth fibre approximation is typically considered in existing effective thermal conductivity analyses in the literature [7,9,11,20,26,38,58] and provides a good grounds for comparison to the rough fibre cases. The solid, dark curve within the grey shaded region represents the arithmetically calculated average total contact area amongst the various rough fibre contact profile combinations. The shaded region represents the range exhibited throughout the analysis, defined by the upper and lower bounds of the total contact area values. The total
contact area for the average rough case and its upper bound are less than the total contact area of smooth fibres in contact. This is observed for the range of angles of orientation and contact forces. The difference in the total contact area for the rough and smooth cases increases with contact force.

3.7.3 Curve-Fitting of Total Contact Area Data

The total contact area is depicted in a contour graph as a function of orientation angle and the contact force in figure 3-11. The data displayed in figure 3-11 is the average contact area amongst the various fibre surface profile contact combinations. As can be seen, the contact area increases with contact force, and decreases with angle of orientation (as the angle of orientation approaches the orthogonal case of 90°). The change in contact area with angle of orientation is more evident for larger contact forces. The average measured rough contact area data, shown in figure 3-11, was surface-fit to obtain an empirical formulation as a function of angle of orientation ($\theta$) and contact force ($F_c$). The form of the empirical average contact area surface-fit ($A_{total,avg}$), measured in $\mu$m², and standard deviation between measured values ($A_{total,std}$) is displayed in equation 3.3.

$$f (\theta, F_c) = \beta_0 + \beta_1 \theta + \beta_2 F_c + \beta_3 \theta^2 + \beta_4 \theta F_c + \beta_5 F_c^2$$

The constants for $A_{total,avg}$ and $A_{total,std}$ are found in table 3-3. The surface fits were determined using a least squares fit (MATLAB 2011a), and were fitted to the data within 98% accuracy. The surface-fits for the average contact area and contact area standard deviation were computed for the angle of orientation range considered (15° to 90°), and contact force range of 0.0001 N to 0.01 N. Note, the units for the input variables $\theta$ and $F_c$ are degrees (°) and newtons (N) respectively. The formulation shown in equation 3.3 and table 3-3 may serve use to
those interested in incorporating fibre surface morphology between rough carbon fibres within the ranges considered. Also, these formulations could be used as an input into existing effective thermal conductivity models to incorporate surface feature information with respect to the carbon fibres.

3.8 Rough Fibre Thermal Contact Resistance

The $TCR$ data for various fibre profiles in contact as a function of contact force and angle of orientation is shown in figure 3-12a and figure 3-12b. As shown in figures 3-12a and 3-12b, the $TCR$ for the average rough fibre contact is greater the smooth fibre case.

3.8.1 Thermal Contact Resistance Range

Similar to figure 3-10, the shaded regions in figure 3-12 represent the range of $TCR$ measured for various fibre contact combinations. The range of rough $TCR$ values (shaded region in figure 3-12a) is large, constituting to approximately 40% of the average $TCR$ when the contact force is greater than 0.008 N, and approximately 90% of the average $TCR$ when the contact forces are below 0.002 N. This is shown specifically in figure 3-12b, where the lower bound of the rough $TCR$ approaches the smooth fibre case for an angle of orientation near 90° and high contact forces. The $TCR$ of the rough GDL fibres in contact is sensitive to the shape of the total contact area; contact areas derived from multiple smaller micro-contacts lead to thermal contact resistances which are higher than those arising from contact areas derived from larger elliptical shapes, leading to the variation in $TCR$ results presented (range of $TCR$ values). It was found that the lower bound of the rough fibre $TCR$ range is defined by fibre profiles with larger asperities in contact, leading to larger micro-contact areas, while the upper bound is defined by fibre profiles with smaller asperities, leading to smaller micro-contact areas.
3.8.2 Critical Regions in GDL with respect to Thermal Contact Resistance

When the contact force is significantly high, the amount of compression of each of the fibres into one another becomes significantly large, and may amount to the heights of the asperities having a minimal effect on the overall $TCR$. In essence, higher contact forces cause compression area shapes that approach the smooth fibre case (elliptical). The opposite is true for lower contact forces, where the surface roughness and asperity heights dominate the contact formed between rough fibres, leading to much larger $TCR$ values. This is significant in the design of GDLs since there will be various contact forces experienced by fibres underneath the bipolar plates. In the regions below the bipolar plate ribs, there will be larger contact forces, and therefore, the effect of fibre surface morphology will be negligible with respect to the computed $TCR$. However, underneath the channels of the bipolar plates, the contact forces will be less, and therefore the fibre roughness should be considered in the determination of the thermal heat transfer between contacting fibres.

3.8.3 Curve-Fitting of Thermal Contact Resistance Data

A contour plot for the thermal contact resistance versus the angle of orientation and contact force is depicted in figure 3-13. The data in the contour plot is calculated similarly to that of figure 3-11, being the arithmetic average of the various fibre profile contact combinations with varying contact force and angle of orientation. The force axis is displayed in a logarithmic fashion, as there are larger gradients in thermal contact resistance for lower contact forces. The $TCR$ tends to increase with decreasing contact force and as the angle of orientation approaches the orthogonal case. Also, the change in $TCR$ with angle of orientation is more evident for contact forces below 0.001 N; an opposite trend to that shown in the contact area contour in
Equation 3.4 shows the empirical form for the effective thermal contact resistance average values \((TCR_{avg})\), measured in \(K(mW)^{-1}\) (degrees kelvin per milliwatt), and the standard deviation \((TCR_{std})\). The standard deviation is calculated similarly to that of contact area standard deviation, \(A_{total, std}\). Empirical formulations for the \(TCR\) were derived using MATLAB, in a similar manner to those derived for the total contact area found in equation 3.3. The coefficients to the two empirical surface-fits are tabulated in table 3-4, and are valid for angles of orientation of 15° to 90°, and contact forces of 0.0001 N to 0.01 N. The formulations shown in equation 3.4 and table 3-4 provide a tool used to reproduce the analysis conducted for rough contact between GDL fibres. It is important to note that the thermal contact resistance reported is solely due to the conduction through the solid space of the contact carbon asperities. Results from the \(TCR\) study may be used in analyses with other materials within the contact region (such as PTFE, binder, or interstitial fluid) causing other thermal contact resistances, though care must be taken in summing the resistance values. The analysis conducted provides insight into the effect of incorporating the circumferential fibre roughness in computed thermal contact resistance, and also provides an alternative to increasing the grid resolution when considering the fibre structures in GDL models.

\[
(3.4) \quad f(\theta, F_c) = C_0 + \theta^{a_0} + F_c^{a_1} + \theta^{a_2}F_c^{a_3} + \exp(a_4F_c)
\]

3.9 Conclusion

In this study, a method for determining the contact area between rough fibres for various angles of orientation and contact load was presented. Fibre surface information was obtained using AFM for untreated Toray carbon paper (TGP-H-120) GDL samples with 0% PTFE content. A modification of the Greenwood rough contact model, treating the asperities as cylindrical tips
(rather than the classical use of spherical tips), was used to determine the contact area between rough fibres. It was found that the contact area of rough fibres housed in the GDL changes with angle of orientation, with minimum values when the contacting fibres are orthogonal. The contact area of rough fibres was found to be less than the analogous smooth fibre case for various angles of orientation and contact force, with larger deviations for higher contact forces.

It was found that the thermal contact resistance decreases with increasing contact force, with maximum points at angles of orientations of 90°. The effect of fibre surface morphology on thermal contact resistance calculations is more significant for lower contact forces, such as those imposed on fibres underneath the bipolar plate channels. Empirical formulations for the contact area and thermal contact resistance were presented, and were found to be within 98% accuracy of the average contacting fibre surface. The goal of this work was to determine the impact of the smooth-fibre assumption, and it was found that the circumferential roughness features do have a significant impact on the contact area and thermal contact resistance between fibres. Fuel cell modellers are encouraged to incorporate these circumferential roughness features into their bulk (macro) GDL models, which should then result in more predictive thermal conductivity values that can be compared to experimental validation work.
### 3.10 Tables

Table 3-1. AFM image surface feature data.

<table>
<thead>
<tr>
<th>AFM Image</th>
<th>RMS Roughness [nm]</th>
<th>Surface Area [µm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>64.794</td>
<td>10.322</td>
</tr>
<tr>
<td>b</td>
<td>50.782</td>
<td>10.427</td>
</tr>
<tr>
<td>c</td>
<td>95.808</td>
<td>11.895</td>
</tr>
<tr>
<td>d</td>
<td>53.864</td>
<td>10.639</td>
</tr>
<tr>
<td>e</td>
<td>23.361</td>
<td>9.807</td>
</tr>
<tr>
<td>f</td>
<td>75.411</td>
<td>11.443</td>
</tr>
</tbody>
</table>
Table 3-2. Properties of the GDL Carbon Fibres

<table>
<thead>
<tr>
<th>Average Fibre Diameter, $d$</th>
<th>Average Fibre Length, $l$</th>
<th>Thermal Conductivity, $k_f$</th>
<th>Poisson’s Ratio, $\nu$</th>
<th>Young’s Modulus of Elasticity, $E_f$</th>
</tr>
</thead>
</table>
Table 3-3. Coefficients matrix for empirical mean total contact area ($\mu m^2$) and total contact area standard deviation formulae.

<table>
<thead>
<tr>
<th>$f$</th>
<th>$\beta_0 \times 10^2$</th>
<th>$-\beta_1 \times 10^3$</th>
<th>$\beta_2$</th>
<th>$\beta_3 \times 10^5$</th>
<th>$-\beta_4 \times 10^1$</th>
<th>$-\beta_5 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{total_avg}$</td>
<td>3.514</td>
<td>3.147</td>
<td>89.41</td>
<td>3.088</td>
<td>3.242</td>
<td>1.681</td>
</tr>
<tr>
<td>$A_{total_std}$</td>
<td>3.585</td>
<td>1.974</td>
<td>35.47</td>
<td>1.817</td>
<td>1.378</td>
<td>0.912</td>
</tr>
</tbody>
</table>
Table 3-4. Coefficients matrix for empirically determined mean thermal contact resistance ($K/(mW)^{-1}$) and thermal contact resistance standard deviation.

<table>
<thead>
<tr>
<th>$f$</th>
<th>$-C_0$</th>
<th>$\alpha_0 \times 10^2$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2 \times 10^2$</th>
<th>$-\alpha_3 \times 10^1$</th>
<th>$\alpha_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$TCR_{avg}$</td>
<td>1.553</td>
<td>1.049</td>
<td>2.98</td>
<td>1.652</td>
<td>1.27</td>
<td>97.42</td>
</tr>
<tr>
<td>$TCR_{std}$</td>
<td>1.327</td>
<td>-6.530</td>
<td>2.50</td>
<td>-0.507</td>
<td>0.98</td>
<td>58.43</td>
</tr>
</tbody>
</table>
Figure 3-1. AFM images used in rough contact analysis featuring cylindrical asperities (image b and image f, respectively), protruding irregularities (image a and image c), localized flat-zones (image e), and sharp peaks (image d).
Figure 3-2. 3D mapping of fibre surface data obtained using AFM for image \( f \).
Figure 3-3. Height deviation in the circumferential (a), and longitudinal (b) directions for AFM image a.
Figure 3-4. Algorithm used to determine thermal contact resistance and contact area for rough contacting fibres.
Figure 3-5. Average Cross-Sections with and without curve fits for AFM images a, c, and f.
Figure 3-6. Comparison of micro-contact shapes for two asperities of radii of curvature equal to 100 nm in contact with various contact force, and angle of orientation equal to (a) 45° and (b) 90°.
Figure 3-7. Qualitative representation of heat transfer between rough fibres.
Figure 3-8. Micro-contact area versus contact force for two AFM image \textit{a} type profiles in contact, for an angle of orientation of (a) 30°, (b) 45°, and (c) 90°.
Figure 3-9. Total Contact Area versus Contact Force for Rough and Smooth Cases
Figure 3-10. Total contact area versus contact force for rough and smooth cases for an angle of orientation of 45° (a), and total contact area versus angle of orientation for rough and smooth cases for a contact force of 0.01 N (b).
Figure 3-11. Average total contact area contour plot versus angle of orientation and fibre contact force.
Figure 3-12. Effective thermal contact resistance versus contact force for rough and smooth cases for an angle of orientation of 45° (a), and effective thermal contact resistance versus angle of orientation for rough and smooth cases for a contact force of 0.01 N (b).
Figure 3-13. Effective Thermal Contact Resistance versus Angle of Orientation and Fibre Contact Force
Chapter 4: Characterization of the MPL

4.1 Introduction

In this chapter, atomic force microscopy (AFM) and scanning electron microscopy (SEM) images of two commercially available MPL materials; SGL-10BB and SGL-10BC, are analyzed for the purpose of determining the impact of nano-scale features on effective thermal conductivity modeling. Particle diameters and the nature of particle contacts were characterized and presented as inputs for future stochastic MPL models. The need for both high-resolution MPL reconstructions and material-specific data regarding MPL nano-features in heat transfer modeling is highlighted in this chapter. Also, a robust model based on the Gauss-Seidel iterative method is presented as a useful technique for analyzing the effective thermal conductivity of multi-phase MPL structures. The results of this study have been presented for the first time in the literature, in the recently submitted journal manuscript [61].

4.2 Motivation and Objective

The MPL is a critical component to the PEM fuel cell that has been shown to enhance cell performance by reducing flooding at the interface between the catalyst layer (CL) and GDL [28], thereby increasing catalyst utilization efficiency for electrochemical energy conversion [34]. Also, the addition of the MPL has been found to decrease water saturation in the cathode of the PEM fuel cell, which improves the ability for inlet gases to reach the reaction site [62] due to its highly hydrophobic nature [8]. However, due to its high polytetrafluoroethylene (PTFE) content, incorporation of an MPL tends to lower the overall effective thermal conductivity of the diffusion media [8]. Therefore, there is a growing interest in optimizing the design of the MPL
structure via computational modeling [21,34] with respect to both water and thermal energy management, even though the batch-to-batch variations and length scale of the MPL features contribute to the challenge of validating numerical models [22].

The MPL structure is a relatively new component in the PEM fuel cell. Effective thermal conductivity models are evolving to more accurately model the material structure. For example, for the case of modeling the GDL, initial effective thermal conductivity models assumed fibres were straight and smooth [5,7,9,20,25,26], however recent studies have found that higher resolution features of the GDL fibres, such as the fibre roughness [47] and waviness [45], should be considered. In previous literature [21,22,34], the nano-features of the MPL (i.e. nature of particle-to-particle contacts) were not considered, though they may have a critical impact on rate of heat transfer in the solid-space. The findings in literature indicate that only the MPL bulk properties, such as agglomeration shape [21,34], porosity [21,34], thickness [34], and penetration depth into the GDL [6,34], have been considered. Also, in these models, generic MPL specifications regarding the particle size and pore-space have been used in the reconstructions, without consideration of MPL structure variability among material types and manufacturers [22].

The motivation of this chapter is to obtain material-specific structural data on the nano-features of SGL-10BB and SGL-10BC, including the particle diameter and nature of particle contact, which will provide fuel cell modelers the reconstruction resolution required to accurately model heat transfer in the MPL. The Gauss-Seidel iterative method is presented as a robust tool which can be applied to multi-phase conductive heat transfer modeling. With the findings in this study, MPL materials can be designed to optimize cell performance with respect to improving the effective thermal conductivity [44].
4.3 Characterization of MPL Materials

As can be seen from the SEM image shown in figure 4-1, the MPL is comprised of particles of various sizes. This is well documented within the literature regarding the MPL, however no data has been published on the quantification of the MPL particle size distribution (to the best of the authors’ knowledge). In order to determine the particle size distribution within the MPL, information regarding the curvature of the particles is required. AFM functioning in *tapping mode* was used to obtain surface information for both SGL-10BB and SGL-10BC. Seven samples of both materials were imaged with an atomic force microscope (Nanoscope IIIa Multimode by Digital Instruments and MFP-3D Infinity by Oxford Instruments). For each sample, images were obtained using a frame size of 1x1 µm². The region of interest was selected to obtain a resolution of 2 nm per pixel for measuring the particle curvature (based the expected particle size [21]). Also, the frame size was based on the results of Wargo et al. [63], where it was found that the representative elementary volume of the MPL based on diffusivity calculations is 1 µm³. An example of the AFM results is shown in figure 4-2.

The results obtained from AFM provide the resolution required to analyze the radii of curvature of the particles, from which the particle size distributions could be obtained. The particle centre coordinates (x- and y-positions) were located by determining the local maxima within the respective AFM binary images. The particles were assumed to be spherical. The centres of adjacent particles, with x- and y-coordinates equal to those of the local maxima, were connected with straight lines, from which the surface height information of the particles was obtained (along the directions connecting the particle centres). The surface height information for over 400 particles was analyzed using the AFM images of SGL-10BB and SGL-10BC.
A smoothing filter was applied to the surface height contours of connecting particles in order to reduce the noise attributed to the AFM measurement (figure 4-3 shows an example). The smoothing filter was applied in MATLAB using the locally weighted scatter plot smooth or loess function, which uses a locally weighted linear regression model to filter the data. A span of 30%, corresponding to the percentage of data points near the data point considered (included in the curve fit calculation), was used reduce the noise attributed to the AFM measurement. Circles were fitted to the curved regions based on the Taubin method [64] in order to find particle diameters and filling radii of particle-particle contacts. An example is shown in figure 4-4, where the curved black line represents the filtered AFM data. I define the particle diameters as the diameter of the circles fitted to the protruding regions of the filtered AFM data. The location of the protruding region was set to the location near the local maxima where the concavity\(^1\) is negative (concave down). The filling radius is defined as the radius of a circle which fits the concave up (positive concavity) regions of the filtered AFM data, forming a particle connection. The particle protrusion and particle connection regions are shown schematically in figure 4-3.

The particle size distributions and filling radius distributions from the 2D height contours are presented in figures 4-5 and 4-6, where the solid line represents gamma-distribution curve fittings. The particle diameter and filling radius distributions for both SGL-10BB and SGL-10BC can be compared in figure 4-7. Table 1 includes the shape parameter and scale parameter, which can be used to reproduce the statistical distributions that can be used as inputs into future stochastic models. As can be seen in figures 4-5 and 4-6, there is a wide range of particle

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\(^1\) Concavity is mathematically defined as the second derivative of the height \(f''(x)\), where \(f(x)\) is concave up at \(x\) if \(f''(x) > 0\), \(f(x)\) is concave down at \(x\) if \(f''(x) < 0\), and \((x, f(x))\) is an inflection point if \(f''(x) = 0\).
diameters and filling radii for both materials. In SGL-10BC, there are large particle sizes as measured with AFM yielding an average particle size of 60.9 nm, compared to 38.4 nm for SGL-10BB (table 1). Although the particle size distributions measured is larger than that documented by Becker in [21,34], the mean particle diameter (for SGL-10BB only) and filling radius agree well with those documented by Becker in [34]. Therefore, the MPL nano-structures are material dependent [22]. Particle size and filling radius distributions can also be obtained for other types of diffusion media, characterizing their material-specific structural properties as well.

### 4.4 Thermal Model

MPL particle structures were generated computationally to reflect the impact of the nature of contact between particles on thermal conduction. The types of structures considered vary the nature of contact between particles, and are shown schematically in figures 4-8 and 4-9. The parameters controlling structural features are discussed in detail in section 4.5. The method used for determining the effective thermal conductivity of various particle contact structures is based on the Gauss-Seidel iterative method. The main mode of heat transfer is conduction between MPL contacts [21,34], since the pores of the MPL are small, and the fluid velocity is low (negligible convection) [58]. Heat transfer via radiation is assumed to be negligible [65] since the operating temperature of the PEM fuel cell is 80°C [5,20]. Therefore the heat transfer between MPL particle structures is modeled as purely conductive in this thesis.

#### 4.4.1 Thermal Model Description

Heat transfer within the MPL particle structures is modeled by discretizing the structures into cubic elements, from with the Gauss-Seidel iterative method (based on Fourier’s law of conduction) is applied. A schematic of a MPL particle structure (not showing the cubic elements
which form it) is included in figure 4-8a, while figure 4-8b includes a single cubic element taken from the structure and its neighbours. Constant temperature boundary conditions were positioned at the top and bottom faces of the modeled MPL particle structure, denoted $T_{\text{top}}$ and $T_{\text{bottom}}$. A linear temperature gradient from the bottom to the top surface was used initially for the intermediate elements in both cases. The element temperatures are calculated and updated until the bottom and top heat fluxes are within 0.1% of each other, which is assumed to simulate steady state conditions and calculation convergence. For the MPL particle structures analyzed in this chapter, insulated boundary conditions were imposed on the four side walls.

The structure analyzed is discretized into cubic elements. Each element has an energy balance comprised of six terms, representing the heat transfer across the different faces of the element (up [U], down [D], north [N], south [S], east [E], and west [W]). Each structure was treated as a two-phase material with a solid-phase and fluid/matrix-phase. The matrix-phases considered were stagnant air with thermal properties equivalent to air at 80°C (operating temperature of PEM fuel cells) [58], representing unsaturated MPL, and liquid water at 80°C, representing saturated regions in the MPL. Equations 4.1-4.3 represent the approach to determining the temperature profile of the structure under consideration, where an individual element temperature is denoted by $T_{\text{element}}$.

\[
(4.1) \quad 0 = \dot{Q}_U + \dot{Q}_D + \dot{Q}_N + \dot{Q}_S + \dot{Q}_E + \dot{Q}_W
\]

Each of the respective heat transfer rates, between the 6 directions shown in equation 4.1, can be calculated using equation 4.2, where $\dot{Q}_i$ represents heat transfer between the element under consideration and neighbouring element $i$ (U, D, N, E, S, W), $d_{\text{voxel}}$ is the voxel width (detailed discussion in section 5.5.2), $A_{\text{voxel}}$ is equal to $d_{\text{voxel}}^2$, and $T_i$ is the temperature of element $i$. 
The conductivity of the considered and neighbouring elements would affect the heat transfer rate: $\dot{Q}_i$. An effective thermal conductivity between neighbouring voxels, $k_{\text{eff,voxel}_i}$, defined in equation 4.3, is therefore used in the analysis.

\begin{equation}
(4.3) \quad k_{\text{eff,voxel}_i} = \frac{2 \cdot k_{\text{element}} k_i}{(k_{\text{element}} + k_i)}
\end{equation}

In equation 4.3, $k_{\text{element}}$ represents the thermal conductivity of the element under consideration, while $k_i$ is the thermal conductivity of the neighbouring element. The thermal conductivity of air as the fluid-phase is 0.03 Wm$^{-1}$K$^{-1}$ [25], while the thermal conductivity of liquid water was modeled at 0.58 Wm$^{-1}$K$^{-1}$ [25]. The thermal conductivity of the solid material ($k_{\text{solid}}$) however depends on the PTFE content of the MPL considered, which is well dispersed throughout the MPL solid-phase; in agreement with the findings of Nanjundappaa in [22]. Therefore, the thermal conductivity for the solid-phase was calculated using equation 4.4, where $k_c$ is the thermal conductivity of carbon (120 Wm$^{-1}$K$^{-1}$), $k_{\text{PTFE}}$ is the thermal conductivity of PTFE (0.649 Wm$^{-1}$K$^{-1}$) [25], and $V_{\text{PTFE}}$ is the volume percentage of PTFE used (5% for both materials). The thermal conductivity for the solid-phase of SGL-10BB and SGL-10BC was determined to be 114 Wm$^{-1}$K$^{-1}$.

\begin{equation}
(4.4) \quad k_{\text{solid}} = (1 - V_{\text{PTFE}})k_c + V_{\text{PTFE}}k_{\text{PTFE}}
\end{equation}

Once the temperature profile of the structure (calculated using equations 4.1 to 4.4) has converged, the effective thermal conductivity of the structure ($k_{\text{eff}}$) can be determined using equation 4.5, where $\dot{Q}_g$ is the conductive heat transfer in the direction of the initial temperature.
gradient. The cross-sectional area of the structure is defined as $A_{\text{unit-cell}}$, while the length of the unit-cell is defined as $L_{\text{unit-cell}}$. The equivalent thermal resistance of the structure, $R$, is calculated using equation 4.6, and shown schematically in figures 4-7 and 4-8 (measured between the centres of the contacting particles).

\[
\hat{Q}_{\text{total}} = \int \hat{Q}_g dA = k_{\text{eff}} \frac{A_{\text{unit-cell}}}{L_{\text{unit-cell}}} (T_{\text{bottom}} - T_{\text{top}})
\]

(4.6) \[ R = \frac{(T_{\text{bottom}} - T_{\text{top}})}{\hat{Q}_{\text{total}}} \]

The effective thermal conductivity will vary in the $x$-, $y$-, and $z$-directions of a structure if it is not symmetric. Therefore, equations 4.1 to 4.5 can be used to determine the other directional effective thermal conductivities by rotating a unit-cell in the prescribed direction. Also, the recognition of symmetry will reduce the number of calculations required to analyze structures. Validation of the Gauss-Seidel iterative method can be found in section 5.6, where the heat transfer in MPL particle unit-cells based on body-centered cubic and face-centered cubic orientations are compared to analytical results.

4.4.2 Thermal Model Assumptions

The main assumptions used in this thermal model are summarized here:

- **Initial Condition:** Linear temperature gradient in the heat transfer direction considered
- **Boundary Conditions:** Insulated side-walls
- **Steady-state, 2-phase, three-dimensional conductive heat transfer**
- **The temperature profile has converged when the bottom and top heat fluxes vary less than 0.1%**
- Convective heat transfer is minimal since fluid velocity in the pore space is low [58]
- Heat transfer by radiation can be assumed to be negligible since the operating temperature is 80°C [65]
- Thermal conductivity of the various phases are constant, and do not change with temperature

4.5 Thermal Analysis of MPL Particle Contact Types

Figure 4-9 shows schematics of the three particle types: varying overlapping distance between particles with a filling radius of 0 nm (figure 4-9a), varying filling radius with zero particle overlap or separation distance (figure 4-9b), and finally, varying separation distance between particles with a constant filling radius (figure 4-9c). The equivalent thermal resistance of the particle contacts were determined using the thermal model described in section 4.4. The particles are assumed to be 50 nm in diameter, approximately equal to the arithmetic average of the mean particle diameters found in section 4.3. In the particle structure shown in figure 4-9c, a filling radius equal to 10.8 nm, the mean of the filling radii found in section 4.3, is used. Both unsaturated (air as the surrounding fluid) and water-saturated (liquid water as the surrounding fluid) MPL particle contacts were considered. Finally, in figure 4-10, particle structures with varying particle diameters (and constant filling radius equal to 10.8 nm and separation distance of 0 nm) are presented. Here one particle is held at a constant diameter (Dia₁) of 50 nm, while the other particle’s diameter (Dia₂) varies from 10 nm to 100 nm; within the range of particle diameters found in section 4.3.
4.5.1 Effect of Varying Overlapping Distance on Equivalent Thermal Resistance

The equivalent thermal resistances of overlapping MPL particles were calculated (figures 4-11 and 4-12), and was found to decrease with increasing overlapping distance and found to be inversely proportional to the contact radius (figure 4-9a). The surrounding fluid thermal conductivity has a larger impact on the calculated equivalent thermal resistance when the contact radius is low, since a larger percentage of thermal energy flows through the fluid-phase in this scenario. Figure 4-11 indicates that the equivalent thermal resistance between particle contacts is sensitive to the overlapping distance; reducing to half when the overlap distance increase to 4 nm from point contact, and decreases at a rate of approximately 75 K(mW)$^{-1}$ per nm when the overlapping distance increases from 4 nm to 12 nm. Therefore, the selection of the overlapping distance in stochastic models must be treated with care, especially when the overlapping distance is less than 4 nm.

4.5.2 Effect of Varying Filling Radius on Equivalent Thermal Resistance

Figure 4-13 and figure 4-14 show the impact of varying the filling radius between particle contacts on equivalent thermal resistance (figure 4-9b) for air and water as the surrounding fluids. The equivalent thermal resistance between particles decreases with increasing filling radius and contact radius, though the change in equivalent thermal resistance tends to plateau when the filling radius reaches 10 nm. The equivalent thermal resistance decreases by 16% when the filling radius changes from 10 nm to 25 nm, compared to the 43% decrease in the equivalent thermal resistance when increasing the filling radius from 1 nm to 10 nm. Therefore, in stochastic MPL models based on experimentally observed data, the selection of a filling radius is
significant when less than 10 nm, and high resolutions should be incorporated into modeling of the MPL particle connections in order to incorporate this effect.

4.5.3 Effect of Varying Separation Distance on Equivalent Thermal Resistance

Figure 4-15 includes the effect of altering the separation distance (figure 4-9c) on the equivalent thermal resistance between MPL particle contacts with a constant filling radius of 10.8 nm. The equivalent thermal resistance increases exponentially with separation distance while being sensitive to the fluid-phase thermal conductivity (figure 4-16). The separation distance is a key parameter required to analyze the heat transfer between particle contacts in the MPL due to its extreme impact on the equivalent thermal resistance. Based on these insights, the predictive model development would benefit from quantifying the particle separation distance in MPL materials. This information can only be obtained using data from a 3-dimensional reconstruction of the MPL materials with nano-resolution.

4.5.4 Effect of Varying Particle Diameter Ratio on Equivalent Thermal Resistance

The effect of varying the particle diameters (for two connected particles) on the equivalent thermal resistance is presented in figure 4-17. A separation distance of 0 nm and a filling radius of 10.8 nm were used in this study. Here the particle diameter ratio (Dia$_1$/Dia$_2$) is shown schematically in figure 4-10, where Dia$_1$ is changed from 10 nm to 100 nm. As Dia$_1$/Dia$_2$ increases, the contact area between the particles increases, causing the equivalent thermal resistance to decrease. The equivalent thermal resistance is sensitive to the Dia$_1$/Dia$_2$ when Dia$_1$/Dia$_2$ < 1, and less sensitive for Dia$_1$/Dia$_2$ > 1.

Using the shape parameters and scale parameters (table 4-1), 10,000 particle pairs representing fictitious particle connections were randomly generated while holding one particle diameter
constant at 38.4 nm (SGL-10BB) or 60.9 nm (SGL-10BC) respectively (material averages). The particle diameter ratios were then computed and summarized in figure 4-18. The average particle diameter ratio for SGL-10BB and SGL-10BC is less than 1. Therefore, assuming 10,000 particle connections is sufficient and considering the results of figure 4-18, it was found that the MPL should not be modeled with constant particle size. However, it is important to note that this analysis has been based on studies involving two particles in contact, and should be extended to multiple particles in contact. Stochastic models should be computed using variable particle sizes to explore the impact on MPL effective thermal conductivity modeling, as the minimum particle size used in the reconstruction will gauge the level of resolution required to accurately model the MPL structure.

The analysis in section 4.5 compares various MPL particle structures and the impact of structural features on the equivalent thermal resistance. Section 4.5 should be used as a tool for future MPL models, helping justify the assumptions used in the construction of the particle-based agglomerations found in the MPL.

4.6 Conclusions

In this study, nano-features of MPL structure were analyzed, and the impact of incorporating those features into equivalent thermal resistance calculations was investigated. It was found that the particle diameters in SGL-10BB are smaller than those in SGL-10BC, having mean diameters of 38.4 nm and 60.9 nm respectively, reflecting variability among material types. The separation and overlapping distance between MPL particles had the largest impact on equivalent thermal resistance. For example, the equivalent thermal resistance between MPL particles was found to decrease by half when the overlapping distance increased to 4 nm from point contact,
while the equivalent thermal resistance increases exponentially with separation distance. Also, the equivalent thermal resistance between MPL particles is sensitive to the filling radius for values less 10 nm and particle diameter ratios less than 1. If these parameters, such as the particle spacing or the filling radius, can be controlled in the fabrication of new MPLs, the effective thermal conductivity can be greatly increased. Also, by incorporating material-specific nano-features in MPL computational reconstructions, the thermal gradients within the MPL can be computed more accurately, and the effective thermal conductivity of the MPL, which has been found to depend on the MPL particle contact [22], can be accurately computed. The results found here are useful inputs to existing and future MPL models, driving them towards more realistic reconstructions of the MPL. The results of this study can assist in the fabrication of better, advanced materials, further improving the efficiency of the technology, driving it towards global commercialization.
4.7 Tables

Table 4-1. Statistical information based on the gamma probability distribution regarding MPL particle contacts and particle connections

<table>
<thead>
<tr>
<th></th>
<th>Particle Diameter</th>
<th></th>
<th>Filling Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SGL-10BB</td>
<td>SGL-10BC</td>
<td>SGL-10BB</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.4 nm</td>
<td>60.9 nm</td>
<td>10.1 nm</td>
</tr>
<tr>
<td>Scale Parameter</td>
<td>10.9</td>
<td>19.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Shape Parameter</td>
<td>3.5</td>
<td>3.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>
4.8 Figures

Figure 4-1. SEM image of SGL-10BC showing variance in particle sizes
Figure 4-2 AFM images of SGL-10BB MPL with frame size of 1x1 μm²; Figure 4-2a) 3-dimensional view, Figure 4-2b) Topological view.
Figure 4-3: Comparison of raw AFM data (SGL-10BB) and smoothed data using a span of 30%.
Figure 4-4. SGL-10BB particles (red) and particle connections (blue) circle fitted to the smoothened AFM image height data (black).
Figure 4-5. Particle size distribution for SGL-10BB (a), and SGL-10BC (b).
Figure 4-6. Filling radius distribution for SGL-10BB (a), and SGL-10BC (b).
Figure 4-7. Combined data for SGL-10BB and SGL-10BC; particle size (a) and filling radius (b)
Figure 4-8. Schematic of MPL particle structure (a) boundary conditions and (b) cubic element
Figure 4-9. Schematic of MPL particle contact types; (a) various overlapping distance with no filling radius, (b) various filling radius with no overlapping or separation distance, and (c) various separation distance with constant filling radius.
Figure 4-10. Schematic (a) and 3D representation (b) of particles with varying diameter in contact. Figure 4-10b shows examples for two Dia₁/Dia₂: 0.4 and 1.6.
Figure 4-11. Equivalent thermal resistance between MPL particle contacts versus overlapping distance.
Figure 4-12. Comparison of equivalent thermal resistance with air and water as the surrounding fluid, versus overlapping distance.
Figure 4-13. Equivalent thermal resistance between MPL particle contacts versus filling radius.
Figure 4-14. Comparison of equivalent thermal resistance with air and water as the surrounding fluid, versus filling radius.
Figure 4-15. Equivalent thermal resistance between MPL particle contacts versus separation distance.
Figure 4-16. Comparison of equivalent thermal resistance with air and water as the surrounding fluid as a function of particle separation distance.
Figure 4-17. Equivalent thermal resistance between MPL particle contacts versus particle diameter ratio (Dia₁/Dia₂)
Figure 4.18. Particle diameter ratio distribution generated using SGL-10BB and SGL-10BC particle size data (figure 4-5)
Chapter 5: Unit-Cell Analysis

5.1 Introduction

In this chapter, I present the preliminary stages of utilizing unit-cell analysis (UCA) as a technique for modeling the MPL particle interactions and agglomeration shapes, for the purpose of modeling the MPL effective thermal conductivity. Various unit-cell structures are constructed using the particle diameter and filling radius distributions of SGL-10BB and SGL-10BC (chapter 4) and are analyzed for their effective thermal conductivity, to be used as building blocks for constructing stochastic or deterministic MPL materials.

5.2 Motivation and Objective

Due to the random nature of the MPL particle agglomerations [66], the variability in the MPL structure [22], and scale of the structural features [21,67], it is difficult to develop an accurate representation of the MPL to measure the effective thermal conductivity. In particular, the resolution required to effectively model the contact region between particles has not been achieved in literature for modeling the solid-space of the MPL [67,68]. Based on the particle diameter and filling radius distributions for SGL-10BB and SGL-10BC (chapter 4), the MPL should be modeled with material-specific inputs regarding the particle size and nature of contact. The current models found in literature are based on the stochastic reconstruction of the entire MPL material [21,34] or deterministic reconstructions of the MPL based on computed tomography [22,67,68]. Incorporating higher resolution information is necessary for modeling heat transfer between MPL particles and nano-pores found between the particles [22] (as discussed in section 4.5), but has been disregarded in the past since the resolution of
computed tomography reconstructions of the MPL are incapable of imaging the nano-structures with such detail [67].

UCA has been used to model the GDL by Sadeghi et al. [7,9,26] who considered fibre interactions to be repeating structures. To the best of the author’s knowledge, the results of this chapter highlight the first time UCA has been used to analyze the effective thermal conductivity of the MPL. Therefore, UCA is presented as a novel technique for analyzing the MPL under the necessary resolution for modeling nano-features in the structure, and provides the ability to parameterize those nano-structural features with respect to effective thermal conductivity calculations, helping further optimize the MPL structure. UCA is based on having MPL modeling being approached into two length scales; nano-scale for particle interactions and agglomerations (via unit-cells), and micro-scale for the modeling of cracks and large pore spaces (not covered in this chapter). Therefore the objective of this study is to obtain unit-cells for SGL-10BB and SGL-10BC that can be used as building blocks to reconstruct the MPL stochastically, or to populate low-resolution material reconstructions which may have been previously viewed as insufficient for modeling heat transfer. A schematic of how UCA can be applied in the construction of nano-resolved MPL structures is shown in figure 5-1 (in 2-dimensions for visualization purposes).

5.3 Unit-Cell Reconstructions of MPL Particles

The unit-cell reconstructions utilized to model MPL particles are based on body-centred cubic (BCC) and face-centred cubic (FCC) orientations. The BCC unit-cell contains particles positioned at the volumetric centre of the unit-cell, and eight corners. The FCC unit-cell is similar to the BCC structure, with eight $1/8$th particles located at the eight corners of the unit-cell,
however, instead of having a particle at the volumetric centre, six half-particles are centred at the six faces of the unit-cell. Visual representations of BCC and FCC structures, assuming point contact, are displayed in figure 5-2, for various unit-cell side lengths, $a$, measured in voxels. Increasing the voxel resolution (side-length of individual voxels [nm/voxel]) used in the unit-cell reconstruction improves the accuracy of the reconstruction (section 5.3.1) and the accuracy of the measured effective thermal conductivity (section 5.3.2).

5.3.1 Voxel Resolution Selection Based On Unit-Cell Reconstruction Accuracy

One of the first considerations in the development of the unit-cells is the resolution used, corresponding to the number of voxels utilized in the reconstruction. As can be seen in figure 5-2, as voxel count increases, related to $a$, the particles appear to be more spherical. The accuracy of the reconstruction can be quantified by using the solid volume fraction, $svf$, which is defined as the amount of solid volume in a unit-cell divided by the total unit-cell volume. Equations 5.1 and 5.2 include the actual solid volume fractions for the BCC and FCC structures, assuming the particle diameters are all equal. The unit-cell side length, $a$, can be measured in terms of the particle radius, $r$, given that the particles are touching along the body-diagonal for BCC structures ($a_{BCC} \sqrt{3} = 4r$), and along the face-diagonal for FCC structures ($a_{FCC} \sqrt{2} = 4r$).

\[
svf_{BCC} = \left(8 \times \frac{1}{8} \times \frac{4}{3} \pi r^3 + \frac{4}{3} \pi r^3\right) / a^3 = \left(\frac{8}{3} \pi r^3 \right) / a^3 = \frac{\pi \sqrt{3}}{8} \approx 0.68
\]

\[
svf_{FCC} = \left(8 \times \frac{1}{8} \times \frac{4}{3} \pi r^3 + 6 \times \frac{1}{2} \times \frac{4}{3} \pi r^3\right) / a^3 = \left(\frac{16}{3} \pi r^3 \right) / a^3 = \frac{\pi \sqrt{2}}{6} \approx 0.74
\]

Table 5-1 shows the $svf$ of the various reconstructions analyzed in figure 5-2 to determine the effect of varying the voxel resolution on the reconstruction accuracy. As the total number of
voxels used in the reconstruction increases, the svf of the unit-cell approaches the actual svf values of 0.68 for BCC and 0.74 for FCC.

5.3.2 Voxel Resolution Selection Based On Effective Thermal Conductivity Measurement

Though increasing the voxel count in the unit-cell reconstruction causes the svfs to approach the analytical values, it is also important to understand the impact of voxel count on the measured effective thermal conductivity ($k_{eff}$). Figure 5-3 shows the impact of increasing the unit-cell voxel count from $51^3$ to $101^3$ (corresponding to an increase in voxel resolution) for BCC and FCC unit-cell reconstructions on the numerically calculated $k_{eff}$. Figure 5-3 uses the thermal model described in section 4.4 to solve for the $k_{eff}$, with a solid thermal conductivity ($k_{solid}$) to matrix-phase thermal conductivity ($k_{matrix}$) ratio equal to 1000. The numerical $k_{eff}$ data is compared with analytical results conducted by Lord Rayleigh and McPhedran et al. [69,70], which are discussed in detail in section 5.5: Validation of the Thermal Model presented in Section 4.4.

As can be seen in figure 5-2, increasing the voxel count not only improved the reconstruction accuracy, but also improved the accuracy of the $k_{eff}$ measurement, showing an average increase in accuracy (compared to the analytical data) of 34% for BCC structures, and 24% for FCC structures. However, it is important to note that the time required for the analysis of the unit-cells increased by approximately 161 times (since the number of computations increased). Therefore although an increase in voxel count from $51^3$ to $101^3$ is justified by the increase in accuracy, a further increase in accuracy, such as from $101^3$ to $501^3$ is not justified (since the results for $101^3$ are already quite accurate). Nonetheless, a voxel count of $101^3$ voxels per unit-cell was used in
all of the reconstructions (including those in section 4.4) with the assumption that the accuracy of the results in figure 5-3 and section 5.6 are sufficient for this study.

5.3.3 Irregular Unit-Cells

In order to form particle agglomerations using unit-cells, BCC and FCC structures with some missing components must also be included. These types of unit-cells are described herein as irregular unit-cells. For the BCC and FCC structures, there can be numerous combinations of removing selected particles from the structures, resulting in many unit-cells. Figure 5-4 and 5-5 represents the distinct cases for BCC and FCC respectively, from which any irregular unit-cell can be obtained by either rotating or flipping any of these structures. When building agglomerations from the irregular unit-cells, the boundary conditions of the neighbouring unit-cells must be compliant. For example, you may have a BCC-Irregular-1 unit-cell beside a BCC-Irregular-2 unit-cell, provided that the corner diameters for both unit-cells are the same. BCC unit-cells could be mixed with FCC unit-cells for the special irregular cases where one of the faces of the FCC unit-cells does not have a face particle. Irregular unit-cells are analyzed with SGL-10BB and SGL-10BC particle diameter and filling radius inputs from section 4.3, in section 5.4.3.

5.4 Comparison of MPL Particle Features on Unit-Cell Effective Thermal Conductivity

UCA is presented as a method for modeling the effective thermal conductivity of the solid-space of SGL-10BB and SGL-10BC, from which material-specific parameters are required for analysis (results of section 4.3). The effective thermal conductivity of various unit-cell configurations informed from AFM data is presented here, where the side-walls of the unit-cells are modeled
using mirror boundary conditions, simulating the effect of having compliant neighbouring unit-cells, rather than the insulated side-wall boundary conditions used in chapter 4.

5.4.1 Filled Contact Algorithm

Until this point in chapter 5, only unit-cells with particles forming point contact have been considered. However, the results of section 4.3 indicate that there is filling volume between particles found in SGL-10BB and SGL-10BC, with curvature equal to the filling radius. The method used to fill in the contacts of the generated unit-cell structures is straightforward. A sphere of radius equal to the filling radius traverses the surface of the particles in the unit-cell, keeping in contact with the particle surfaces. The sphere is not allowed to overlap any of the solid-space. The regions that the sphere cannot reach, due to the surfaces of the particles being too close together, is converted into solid material. The end result is that the contact regions between particles are filled with solid volume maintaining a curvature equal to the filling radius. A visual example of this is shown in figure 4-9b and figure 4-9c.

5.4.2 SGL-10BB and SGL-10BC Regular Unit-Cells

The parameters used for the BCC and FCC reconstructions of SGL-10BB and SGL-10BC unit-cells, in particular the particle diameter and filling radius, are the mean values included in table 4-1. Since the actual separation/overlapping distance cannot be determined via AFM, the particle configurations built have been parameterized with two extremes: a separation distance equal to the filling radius of the material or a separation distance equal to zero. The unit-cell reconstructions for SGL-10BB, which are similar in shape to SGL-10BC, can be viewed in figure 5-6 for both separation distances. It is important to note that the images shown here show the full particles at the unit-cells face boundaries for visualization purposes. The actual modeled
unit-cells contain $1/8$th particles at the corners (BCC or FCC), and half-particles at the faces (FCC).

As mentioned in section 5.3.2, the unit-cells were discretized with $a$ equal to 101 voxels with equal particle diameters. Based on the characteristic equations for BCC and FCC unit-cells, $a$ [nm] could be obtained through the use of equations 5.3 and 5.4, for BCC and FCC configurations respectively, where $d_s$ is the separation distance between particles. The voxel resolution is defined as $a$ [nm] divided by 101 voxels. Table 5-2 includes the voxel resolution for the various material-specific unit-cells constructed.

\[
(5.3) \quad a_{BCC} \sqrt{3} = 4r + 2d_s
\]

\[
(5.4) \quad a_{FCC} \sqrt{2} = 4r + 2d_s
\]

Using the method described in section 4.4, the SGL-10BB and SGL-10BC BCC and FCC unit-cells were analyzed for their $k_{eff}$, assuming the cells were both unsaturated (table 5-3) and saturated with liquid water (table 5-4). The $k_{eff}$ of the unit-cells vary significantly with the separation distance; in agreement with the findings from section 4.5.3, highlighting the sensitivity of the MPL $k_{eff}$ to $d_s$. Also, the $k_{eff}$ of the unit-cells is dominated by the solid-phase thermal conductivity, varying little with the fluid-phase thermal conductivity. This is mainly due to the high solid volume fractions seen for these unit-cell configurations, where the effect of fluid-phase thermal conductivity will be more significant for irregular unit-cells missing a large number of particles (figures 5-6 and 5-7). The $k_{eff}$ of the BCC structures are less than that of the FCC structures, again since there are higher solid volume fractions in FCC and better solid path connectedness in FCC than in BCC. Finally there are slightly higher $k_{eff}$ values in SGL-10BB
compared to SGL-10BC [6], with an average of 5% higher effective thermal conductivity in SGL-10BB than in SGL-10BC for BCC, and an average of 0.6% higher effective thermal conductivity in SGL-10BB than in SGL-10BC for FCC. This result is affected by the variance in the structures which are dictated by the particle diameters and filling radii, forming a larger particle contact area to particle diameter ratio in SGL-10BB than in SGL-10BC, which causes SGL-10BB to conduct heat better than SGL-10BC within the unit-cells.

5.4.3 SGL-10BB and SGL-10BC Irregular Unit-Cells

In order to model the MPL particle agglomerations for SGL-10BB and SGL-10BC materials, irregular unit-cells based on the material specific nano-features (table 4-1) are required. The complete irregular unit-cell study should incorporate the following combinations:

- SGL-10BB and SGL-10BC nano-features
- Water-saturated and unsaturated MPL unit-cells
- BCC and FCC configurations

Ten different irregular unit-cells for the BCC configuration and sixteen distinct irregular unit-cells for the FCC configuration were generated. Each of the irregular unit-cells must be analyzed in the x-, y-, and z-directions. Also, since the exact separation distance is unknown, the two extremes analyzed in section 5.4.2 must be used in the two different irregular unit-cell reconstructions. This constitutes to 624 simulations that must be conducted to fully characterize the SGL-10BB and SGL-10BC materials (which can be reduced by half if the separation distance of the MPLs is determined, and computed more efficiently using the notion of symmetry in the heat transfer analysis). Since, in section 5.4.2, the effective thermal conductivity of SGL-10BB and SGL-10BC structures do not vary significantly, the effective thermal conductivity of
SGL-10BB BCC and FCC structures is presented with air as the fluid-phase thermal conductivity and particle-to-particle separation distance of 0 nm. It is hypothesized that the effective thermal conductivity will be affected more greatly by the fluid-phase thermal conductivity for irregular unit-cells with lower syfs, which will be the focus of future work in this area of research.

5.4.3.1 Irregular Unit-Cell Nomenclature

The irregular unit-cell reconstructions are based on the structures discussed in section 5.3.3, with material information corresponding to SGL-10BB in table 4-1. The effective thermal conductivities of unsaturated SGL-10BB BCC and FCC with a separation distance of 0 nm can be found in tables 5-5 and 5-6, respectively. In order to decipher the x-, y-, and z-directions with respect to the irregular unit-cells, a naming system has been created. The names of the various irregular unit-cells can be found in tables 5-5 for BCC and 5-6 for FCC, under the irregular unit-cell number in the “Name” rows. The names given to the irregular unit-cells can be used in combination with figure 5-7, which contains labels for the particles in different lattice locations, to determine the directional effective thermal conductivity. The names in tables 5-5 and 5-6 correspond to the particles not present at the particular lattice locations. For example, BCC-Irregular-3 contains two missing particles at opposite corners on one face of the unit-cell. The analogous name for BCC-Irregular-3 is “B4”. Similarly, FCC-Irregular-6 has one face with no particles positioned, and is therefore named “BDQ24”, corresponding to the four corner and one face particles missing. This naming system helps us distinguish the x-, y-, and z-directions of the irregular unit-cells using figure 5-7, which cannot be understood with only figures 5-6 and 5-7, since the images in these figures have been rotated for visualization purposes.
5.4.3.2 Irregular Unit-Cell Effective Thermal Conductivity

As can be seen in the data in tables 5-5 and 5-6, as the number of removed particles increases, the effective thermal conductivity decreases, converging towards the fluid-phase thermal conductivity, which is 0.03 Wm$^{-1}$K$^{-1}$ for air. A significant decrease in effective thermal conductivity occurs when there is not solid material connecting opposite faces (in the direction considered). This is due to the relatively low thermal conductivity of the fluid-phase acting as a thermal insulator, causing the effective thermal conductivity of the unit-cell to decrease significantly. This is seen in between FCC-Irregular-5 (BDQ2) and FCC-Irregular-6 (BDQ24) for example, where the effective thermal conductivity in the $y$-direction decreases from 4.99 Wm$^{-1}$K$^{-1}$ to 0.19 Wm$^{-1}$K$^{-1}$, since the opposite faces with normal parallel to the $y$-direction are no longer connected with solid material, as the particle in the “4” location is removed (evolving from FCC-Irregular-5 to FCC-Irregular-6). Similar trends are found for BCC and FCC structures, when certain lattice locations do not have a particle.

5.5 Validation of the Thermal Model presented in Section 4.4

The thermal model presented in section 4.4 was tested using BCC and FCC structures in point contact, due to their complicated structures and complex thermal gradient patterns arising during convergence of the temperature field. The numerical results from such unit-cells were compared with analytical results presented in [69] by Rayleigh. Rayleigh determined the $k_{eff}$ of BCC and FCC structures of constant particle diameter. Various svfs were analyzed, with limiting cases for BCC and FCC being 0.68 and 0.74, as explored in equations 5.1 and 5.2 respectively. In the mathematical formulations conducted by McPhedran [70], who advanced Rayleigh’s work, the ratio between the $k_{solids}$ to fluid/matrix-phase thermal conductivity $k_{matrix}$ was assumed to be
infinite. Figure 5-8 includes a comparison of the numerical results conducted in this study with the analytical data found in literature, for BCC and FCC structures.

In figure 5-8, the effective thermal conductivity to matrix-phase thermal conductivity ratio is shown as a function of \( svf \). Two \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} \) values were analyzed. The first ratio used the thermal conductivity of air at 80°C (0.03 Wm\(^{-1}\)K\(^{-1}\)) as \( k_{\text{matrix}} \) and the \( k_{\text{solid}} \) of SGL-10BB (114 Wm\(^{-1}\)K\(^{-1}\)), as calculated with equation 4.4. The second ratio used \( k_{\text{solid}} = 100 \) Wm\(^{-1}\)K\(^{-1}\) while the \( k_{\text{matrix}} \) was set to be 0.1 Wm\(^{-1}\)K\(^{-1}\), leading to a \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} = 1000 \). The results obtained for the two respective \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} \) ratios varied by less than 1% for BCC and less than 5% for FCC. This is in agreement with a study conducted by Jae Kim et al. [71], who determined that a \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} > 1000 \) can be viewed as \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} = \infty \). Jae Kim conducted a secondary study for non-infinite \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} \) [71]. Included in figure 5-9 are numerical results for a \( \frac{k_{\text{solid}}}{k_{\text{matrix}}} = 100 \), which can be compared to the study conducted in [71]. Nonetheless, the results give good agreement with the analytically determined data, obtained by Rayleigh [69], McPhedran [70] and Jae Kim et al. [71].

5.6 Conclusion

In this chapter, a model capable of analyzing the MPL of the PEM fuel cell was developed, capable of solving issues regarding reconstruction resolution and computational inefficiencies. Unit-cell analysis was used to analyze the effect of varying MPL structures, SGL-10BB and SGL-10BC, in terms of effective thermal conductivity. It was found that the structures of SGL-10BB are slightly more thermally conductive than SGL-10BC. It was also found that the fluid-phase effective thermal conductivity is not a major contributor in the effective thermal conductivity of regularly shaped BCC and FCC unit-cells, due to the high conductivity of the
solid-phase. The analysis of irregular unit-cells have been presented, and offers a promising, novel approach to modeling MPL materials, provided that the particle diameter, filling radius, and separation distance are known. UCA is a modeling tool that can help in the design of the MPLs at the nano-scale, from which parameters involved in the fabrication can be altered, in order to optimize the structure in terms of thermal energy transfer in the MPL, further improving the efficiency of the technology.
5.7 Tables

Table 5-1. Impact of voxel resolution on accuracy of BCC and FCC reconstruction

<table>
<thead>
<tr>
<th>Unit Cell Width, (a) [voxels]</th>
<th>11</th>
<th>51</th>
<th>101</th>
<th>501</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Voxels</td>
<td>(10^3)</td>
<td>(10^6)</td>
<td>(10^7)</td>
<td>(10^8)</td>
<td>(\infty)</td>
</tr>
<tr>
<td>(svf) (BCC)</td>
<td>0.83</td>
<td>0.79</td>
<td>0.71</td>
<td>0.684</td>
<td>0.68</td>
</tr>
<tr>
<td>(svf) (FCC)</td>
<td>0.89</td>
<td>0.86</td>
<td>0.79</td>
<td>0.749</td>
<td>0.74</td>
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</table>
Table 5-2. Voxel resolution for various unit-cell reconstructions

<table>
<thead>
<tr>
<th>Voxel Resolution [nm/voxel]</th>
<th>SGL-10BB</th>
<th>SGL-10BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>0.55</td>
<td>0.84</td>
</tr>
<tr>
<td>FCC</td>
<td>0.68</td>
<td>1.00</td>
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Table 5-3. Effective thermal conductivity of various unit-cell configurations with air at 80°C as the fluid-phase

<table>
<thead>
<tr>
<th>$k_{\text{eff}} \text{[Wm}^{-1}\text{K}^{-1}]$</th>
<th>$d_s = \text{filling radius [nm]}$</th>
<th>$d_s = 0 \text{ nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SGL-10BB</td>
<td>SGL-10BC</td>
</tr>
<tr>
<td>BCC</td>
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<td>6.62</td>
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<tr>
<td>FCC</td>
<td>11.09</td>
<td>10.97</td>
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</table>
Table 5-4. Effective thermal conductivity of various unit-cell configurations with liquid water as the fluid-phase

<table>
<thead>
<tr>
<th>$k_{\text{eff}}$ [Wm$^{-1}$K$^{-1}$]</th>
<th>$d_s = \text{filling radius [nm]}$</th>
<th>$d_s = 0 \text{ nm}$</th>
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</thead>
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<tr>
<td></td>
<td>SGL-10BB</td>
<td>SGL-10BC</td>
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<td>BCC</td>
<td>7.37</td>
<td>6.99</td>
</tr>
<tr>
<td>FCC</td>
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<td>11.23</td>
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</table>
Table 5-5. Effective thermal conductivity (Wm\(^{-1}\)K\(^{-1}\)) of unsaturated SGL-10BB irregular BCC structures, with a separation distance of 0 nm in x-, y-, and z-directions.

<table>
<thead>
<tr>
<th>Name</th>
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<th>Irregular-3</th>
<th>Irregular-4</th>
<th>Irregular-5</th>
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<td></td>
<td>B</td>
<td>BD</td>
<td>B4</td>
<td>BD2</td>
<td>BD24</td>
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<tr>
<td>(k_{\text{eff}, \text{x}})</td>
<td>8.51</td>
<td>7.44</td>
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<td>5.67</td>
<td>BD24</td>
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<td>(k_{\text{eff}, \text{y}})</td>
<td>8.51</td>
<td>7.44</td>
<td>5.81</td>
<td>5.67</td>
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<td>(k_{\text{eff}, \text{z}})</td>
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<td>BD24XA</td>
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<td>BD24XAC</td>
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<td>0.05</td>
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</table>
Table 5-6. Effective thermal conductivity (Wm\(^{-1}\)K\(^{-1}\)) of unsaturated SGL-10BB irregular FCC structures, with a separation distance of 0 nm in x-, y-, and z-directions.

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<td>BDQ</td>
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<td>(k_{\text{eff}}, x)</td>
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<td>8.84</td>
<td>8.77</td>
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<tr>
<td>(k_{\text{eff}}, y)</td>
<td>12.73</td>
<td>9.09</td>
<td>8.84</td>
<td>8.77</td>
</tr>
<tr>
<td>(k_{\text{eff}}, z)</td>
<td>12.73</td>
<td>9.64</td>
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<td>BDQ24R</td>
<td>BDQ24RT</td>
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<tr>
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<td>8.36</td>
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<tr>
<td>(k_{\text{eff}}, y)</td>
<td>4.99</td>
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<td>(k_{\text{eff}}, z)</td>
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<td>8.12</td>
<td>10.82</td>
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<td>BDQ24RSUT</td>
<td>BDQ24RSUTA</td>
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<td>4.27</td>
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<td>0.18</td>
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<tr>
<td>(k_{\text{eff}}, z)</td>
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<td>6.01</td>
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<tr>
<td>(k_{\text{eff}}, z)</td>
<td>2.30</td>
<td>3.15</td>
<td>0.09</td>
<td>0.07</td>
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</table>
5.8 Figures

Figure 5-1. Schematic of an MPL cross-section, approximately 1 µm by 1 µm, showing the use of unit-cells for population low-resolution MPL reconstructions in 2D: (a) schematic of an MPL cross-section, (b) schematic of a unit-cell populated cross section, and (c) both images overlaid.
Figure 5-2. BCC and FCC reconstructions using various number of voxels
Figure 5-3. Comparison of voxel count in unit-cell reconstruction with analytical results for $k_p/k_m = 1000$ [70], for (a) BCC and (b) FCC structures.
<table>
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<th>BCC-Irregular-1</th>
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<th>BCC-Irregular-3</th>
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</table>

Figure 5-4. Irregular BCC Lattice Structures
<table>
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<th>FCC-Irregular-4</th>
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<td>FCC-Irregular-11</td>
<td>FCC-Irregular-12</td>
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Figure 5-5. Irregular BCC Lattice Structures
Figure 5-6. Various SGL-10BB unit-cell configurations, (a) BCC with $d_s = 10.1$ nm, (b) BCC with $d_s = 0$ nm, (c) FCC with $d_s = 10.1$ nm, and (d) FCC with $d_s = 0$ nm
Figure 5-7. Naming system and co-ordinate axis used to define directional effective thermal conductivities of irregular BCC (a) and FCC (b) unit-cells.
Figure 5-8. Comparison of numerical results with analytical data \cite{69,70}, for various $k_{\text{solid}}/k_{\text{matrix}}$, (a) BCC and (b) FCC.
Figure 5-9. Analytical and numerical results [71] for $k_{\text{solid}}/k_{\text{matrix}} = 100$ (non-infinite), (a) BCC and (b) FCC.
Chapter 6: Conclusions

In this thesis, the effect of incorporating high resolution structural features in the MPL and GDL has been studied to determine the impact on heat transfer modeling in the cathode of the PEM fuel cell. A literature review regarding the role of the GDL and MPL on thermal energy management and water management in the PEM fuel cell has been completed. A comprehensive comparison of literature comparing/contrasting the GDL, MPL, and combined GDL+MPL substrates (both numerically and experimentally) has been included, highlighting the main parameters affecting the bulk effective thermal conductivity measurement.

In chapter 3, the impact of fibre surface morphology on the thermal contact resistance between rough GDL fibres is presented. Carbon fibres housed in untreated Toray GDL were imaged using AFM to obtain their circumferential roughness. The fibre surface asperities were curve fitted and applied to an analytical model based on the Greenwood algorithm for rough contact. The thermal contact resistance between rough contact fibres was calculated using thermal spreading and constriction resistance equations presented in [57], identifying the validity of the smooth fibre assumption. In summary:

- Rough fibre contact results in smaller contact areas than in smooth fibre contact, with both rough and smooth fibre contact area increasing with contact force. The contact area between rough or smooth fibres is minimal when the fibres in contact are orthogonal to each other.

- The thermal contact resistance mean and range decreases with increasing contact force. The upper bound of the thermal contact resistance range is attributed to rough fibres
having asperities with smaller diameters, resulting in smaller micro-contact areas, while the lower bound corresponds to asperities with larger diameters, resulting in larger micro-contact areas.

- The impact of incorporating fibre surface morphology into thermal contact resistance modeling is critical when the contact forces between the fibres are low, deeming the smooth fibre assumption unacceptable for low contact forces. When the contact force is low, the measured thermal contact resistance is much higher in the rough contact case than in the smooth contact case. This corresponds to regions under the bipolar plate channel for example, or any location where there is lower contact force between GDL fibres.

- When the contact forces are high, the rough fibre contact and smooth fibre contact are similar. For example, when the contact force is 0.01 N, the rough thermal contact resistance differs from the smooth fibre contact resistance by approximately 10%.

In chapter 4, commercially available MPL materials, SGL-10BB and SGL-10BC, were characterized with respect to their nano-structures. A curve-fitting algorithm based on the Taubin method was implemented to measure the curvature of particles, and regions between particles, corresponding to particle connections. In this chapter, a thermal model based on the Gauss-Seidel iterative method was also introduced, which has the advantage of modeling the conductive heat transfer within any multi-phase structure given only the structural data of the material considered (a direct output from AFM). The Gauss-Seidel iterative method was used to analyze various types of particle contact with respect to their impact on heat transfer between MPL particles, with a resolution of 0.5 nm/voxel side length, where the critical sizes of particle contact were found. The main conclusions of this chapter are as follows:
The average particle diameter in SGL-10BB was found to be 38.4 nm, which is 37% less than the average particle size of SGL-10BC; 60.9 nm. The nano-features of these two MPL materials vary significantly, as mentioned by Nanjundappa in [22]. Therefore there is a need for characterizing the MPL nano-features for inputs into modeling of specific MPL structures.

The filling radius between particle contacts was found to vary less than the particle diameter; 10.1 nm for SGL-10BB and 11.5 nm for SGL-10BC.

The equivalent thermal resistance between MPL particle contacts is dependent on the contact area and contact shape. The equivalent thermal resistance:

- decreases with increasing overlapping distance; showing an directly inverse proportionality to the contact area between particles
- decreases with increasing filling radius; non-linearly for filling radii less than 10 nm and approximately linearly for filling radii between 10 nm to 25 nm
- increases with increasing separation distance; showing a need for better understanding of the MPL particle separation distances found in MPL materials
- decreases with increasing particle diameter ratio, being more sensitive to \( \text{Dia}_1/\text{Dia}_2 < 1 \) (found in SGL-10BB and SGL-10BC) than \( \text{Dia}_1/\text{Dia}_2 < 1 \).

The MPL should be modeled with variable particle diameter, and variable filling radius, informed by material-specific characterizations.

In chapter 5, UCA is presented as a technique which can be used in future stochastic models of the MPL, considering the nano-features studied in chapter 4. The advantage of using unit-cells in the construction of MPL structures is that a higher resolution can be used to model the MPL particle contacts. With higher resolution reconstructions, the nano-features which affect the
effective thermal conductivity measurement can be considered. Also, unit-cells can be incorporated into existing reconstructions of the MPL to improve their resolution, to be applicable to effective thermal conductivity measurement. The notion of unit-cells can be extended to electrical conductivity or to calculate diffusive properties as well. The following are key-points highlighted in chapter 5:

- BCC and FCC structures were used to model particle unit-cells based on SGL-10BB and SGL-10BC MPL materials. It was found that a voxel side length of 101 voxels sufficiently represents the unit-cell structure with respect to the accuracy of the solid volume fraction measurement, and also effective thermal conductivity measurement. As the number of voxels used in the reconstruction increases, the computational time required to analyze the unit-cell increases significantly.

- The effective thermal conductivity of SGL-10BB and SGL-10BC regular unit-cells with either air or water was computed for two particle separation distances: equal to the fillings radius of the material (via chapter 4) or equal to zero. It was found that:
  
  o The separation distance used to model the unit-cells greatly affects the measured effective thermal conductivity, highlighting the need for the separation distance distribution in SGL-10BB and SGL-10BC materials (unattainable via AFM)
  
  o The effective thermal conductivity of the regular unit-cells is not sensitive to the fluid-phase effective thermal conductivity since the solid volume fractions are quite high in BCC and FCC structures
  
  o SGL-10BB structures are slightly more conductive (0.6% to 5% more) than SGL-10BC structures
• Irregular unit-cells were modeled for their effective thermal conductivity. The irregular unit-cells can be used to generate random, abnormal agglomerations. It was found that the effective thermal conductivity of the irregular unit-cells is directly related to the solid volume fraction of the unit-cell and the solid path connectedness between opposite sides of the unit-cell.

The results of chapters 3 to 5 provide insight as to how future effective thermal conductivity models could be improved to incorporate the effect of circumferential fibre roughness in the GDL and nano-features in the MPL structures, which have been found to effect the conductivity measurement. By improving the accuracy of material models, modeling could be used to better predict the impact of distinct structure alterations, helping guide the design process of PEM fuel cell materials.
Chapter 7: Future Work

The findings in this thesis can be investigated further to either improve the accuracy of thermal conductivity modeling or to explore new concepts, such as those described below.

7.1 GDL Fibre Surface Morphology

The study presented in chapter 3 is based on characterizing the surface of GDL fibres in order to determine the impact of fibre surface morphology on the fibre-fibre thermal contact resistance. Firstly, the carbon fibres analyzed in chapter 3 were from untreated (no PTFE) GDLs. The analysis of PTFE-treated carbon fibres could be insightful to model PTFE-treated GDLs, by investigating the effect of fibre roughness and PTFE content. Longitudinal roughness could be implemented into the study, as it was assumed that the longitudinal roughness is negligible with respect to the circumferential roughness. Also, angles of orientation less than 15° could be analyzed, including the 0° case of line contact between fibres (fibres with parallel central axis, forming contact areas that appear rectangular rather than elliptical). Angles less than 15° were not studied in this thesis as the AFM data was obtained for a 3 µm by 3 µm frame, and shallow angles caused the elliptical contact shape to become longer than 3 µm for high contact forces. Therefore using larger AFM images, contact between rough fibres having shallower angles could be analyzed. Also, the thermal contact resistance between rough fibres and the bipolar plate could be analyzed in collaboration with the results of the fibre waviness study presented in [45], to investigate the impact of fibre roughness in the circumferential direction on the bipolar plate-GDL thermal contact resistance. The results of this study can also be extended to filtration systems comprised of micro-sized fibres, with heat transfer being the limiting factor in the filter performance.
In the contact model of chapter 3, it was assumed that the fibres are supported firmly between the adjacent fibre layers. Therefore, only vertical compression between contacting fibres was considered, which may over-predict the maximum pressure in the fibre. It is important to note that if the maximum pressure exceeds the ultimate compressive strength of 2.88 GPa for carbon fibre, the fibre will fracture [72]. In a future study, the effect of fibre bending could be incorporated to determine the impact of the wrapping angle of contact fibres on the contact area, which would cause the contact area to increase without necessarily increasing the maximum pressure (the pressures in this study may have been overestimated compared to what actually occurs). The effect of bending can be incorporated into Hertzian analysis by determining the curvature of the central axis of the fibres [53]. Once the mechanics of the fibre contact is fully characterized, carbon fibre fracture can be considered.

Finally, future experimental validation could include the following approaches. Though outside the scope of the work presented here, the fibre-to-fibre contact resistance could be measured directly; data for which does not currently exist in the literature. Also, this model could be incorporated into a macro model, such as [7,25,37], and compared to experimentally measured bulk GDL thermal contact resistances reported by [52]. Though this does not constitute as a quantitative validation method, the shape of the TCR vs. Contact Force data (figure 3-12a) does reflect the trends of the contact resistance between the rough MPL-CL interface found by Swamy et al. [33].

**7.2 MPL Particle Analysis**

In the characterization process of SGL-10BB and SGL-10BC, it was assumed that the particles are spherical in nature. The particles imaged via AFM could be curve fitted in two directions to
study the eccentricity of the particles, and how much they vary from the spherical approximation. Also, it was assumed that the particle size and filling radii distributions for the bulk of the MPL could be approximated using the concave down and concave up regions (respectively) of the AFM data obtained for the MPL surface. The tip used in the characterization processes is the AC160TS-R3 model, developed by Asylum Research. In future works, various tip shapes and apex sizes used in the AFM measurement should be studied, in order to determine the dependence of the MPL imaging accuracy on the tip selection and tip wear from repeated operation [73]. Parameters defining the geometry of the tip, such as the tip radius of curvature or the sharpness of the tip (limiting the depth of crevices which can be measured), will have an impact on the resolution of the AFM data. Finally, high resolution 3-dimensional reconstructions based on computed tomography of SGL-10BB and SGL-10BC should be implemented to validate the distributions obtained in this thesis, and also used to compute the separation distance between particles; a necessary input for modelling heat transfer in the MPL. The characterization of other MPL materials could also be completed to fully characterize all types of MPLs.

7.3 Unit-Cell Analysis

In chapter 5, UCA was presented as a tool for which high resolution MPL nano-features could be implemented into a macro-MPL model, assisting in the parameterization of the MPL nano-features on the bulk effective thermal conductivity. Though the unit-cells have been constructed for one case of irregular unit-cells (SGL-10BB with air as the fluid-phase and a separation distance of zero nm), future work involves the full analysis of the SGL-10BB and SGL-10BC, saturated and unsaturated, irregular unit-cells. However before this can be done, the separation distance between MPL particles is required. Also, it is assumed that all of the particle diameters and filling radii could be approximated using the mean values. The effect of varying
the particle diameter and filling radius should also be quantified using UCA, prior to being implemented into a macro-reconstruction of the MPL. It was also assumed that the MPL structure can be modeled as a 2-phase material; the surrounding fluid-phase and solid-phase. The MPL structure should be analyzed at the nano-scale to understand how the PTFE and carbon particles interact to form the solid-space. When this analysis is complete, the UCA could be extended to incorporate 3-phases, differentiating between the PTFE and carbon regions in the solid-space, better approximating the MPL structure.

Finally, a method for incorporating the unit-cell structures must be developed before the unit-cells can be used to model the MPL bulk properties. Wargo et al. determined that the representative elementary volume of the MPL is $1 \mu m^3$ based on diffusivity measurements [63], consisting of approximately $10^3$ unit-cells. Two potential techniques could be used to construct the MPL material:

1. Building the MPL structure randomly while ensuring neighbouring unit-cells have similar faces. The construction of the bulk material could be informed by the pore size distributions of SGL-10BB or SGL-10BC, or the bulk effective thermal conductivity of the MPL materials, presented in table 2-1.

2. Using a lower resolution 3-dimensional reconstruction of the MPL material, and populating the solid-space of the reconstruction with unit-cells. This technique recycles data which may have been seen as unfit for modeling the effective thermal conductivity of the MPL, due to the resolution of the reconstruction not being able to image the nano-contacts between particles. An example of this method is shown schematically in figure 5-1.
By advancing the work of this thesis, fuel cell materials will be able to be modeled more accurately. This will lead to better predictive models for guiding future designs of the cathode materials. Since all of the processes in PEM fuel cell operation are dependent on the material structures, optimally designing them can significantly improve the performance of this promising technology. The works of this thesis can also be extended to the characterization of other applications involving porous media, such as foams, filters, etc.
References


